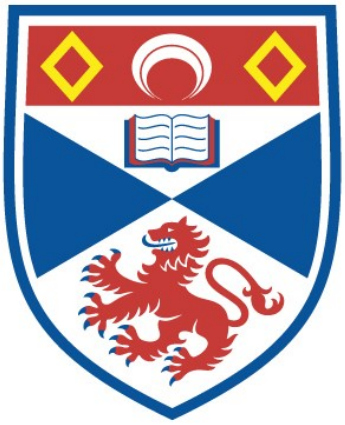
A THERMODYNAMIC STUDY OF THE SULPHATES AND RELATED COMPOUNDS OF ALKALI AND ALKALINE EARTH METALS AT HIGH TEMPERATURES

David Guy Powell

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1971

A THERMODYNAMIC STUDY OF THE SULPHATES AND RELATED COMPOUNDS OF ALKALI AND ALKALINE EARTH METALS AT HIGH TEMPERATURES

A Thesis

presented for the degree of

DOCTOR OF PHILOSOPHY

in the Faculty of Science of the

University of St. Andrews

by

DAVID GUY POWELL M.Sc.

1971

CERTIFICATE

I hereby certify that David Powell has spent eleven terms of research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

P.A.H. Wyatt

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself and that it has not been submitted in any previous application for a Higher Degree.

This thesis describes the results of research carried out at the Chemistry Department, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Professor P.A.H. Wyatt since 1st November 1968.

DAVID G. POWELL

ACKNOWLEDGEMENTS

I wish to thank the British Glass Industry Research Association for financial support during the course of this work.

I am indebted to Pilkington Brothers and the Central Electricity Research Laboratory for making available items of equipment. I am especially grateful to Dr. Kirkbride and Dr. Williams of Pilkington Bros., and Dr. Bowles and Dr. Halstead of CERL for helpful discussions. My thanks are also due to the technical staff of the Chemistry Department, and to Mrs. Cooper who typed this thesis.

Finally I would like to thank my supervisor. Professor Wyatt has been an unfailing source of encouragement and inspiration throughout my tenure, I acknowledge without reservation my debt to him and the profit I have gained by our association.

CONTENTS

INTRODUCTION

The vapour pressures of various salts have been investigated at high temperatures and the results are presented here together with the values found by previous investigators.. Sodium sulphate is extensively used in the glass producing industry and it is in this compound that interest is centred. Other salts have been included in this study for the purpose of comparison. The use made of sodium sulphate in glass making is discussed briefly below. Work previously reported on the determination of the vapour pressure of sodium sulphate will be shown during the course of this introduction to have produced confusing results, and it was for the purpose of introducing some harmony into the sometimes discordant evidence that the present work was undertaken.

The function of sodium sulphate in glass making

Sodium sulphate is a component of the raw material mixture ("glass batch") introduced into glass making furnaces. The sodium sulphate is a fining agent, which helps in the dissolution of batch particles and the dissipation of any gas bubbles formed in the process. Qualitative descriptions of the action of sodium sulphate have been produced by Buss[1] and Conroy et al[2]

with the aid of hot stage microscopes. The wetting of the reacting materials by fluxing agents is apparently more favourable in a melt containing sulphate. With insufficient wetting "dry sand groups" form with the participation of lime and dolomite which sinter together and are dispersed throughout the melt as insoluble remains. At temperatures above that of the formation of the first permanent silicate phase, about 1040°C, sodium sulphate is almost completely insoluble in the glass and collects at all melt-solid and melt-gas interfaces. Due to the presence of this highly fluid sulphate liquid at these interfaces the solid aggregates are broken up and dissolution of solid batch particles proceeds at an increased rate and gas bubbles are expelled more rapidly from the melt. In fact this aspect of sulphate behaviour is in some respects reminiscent of that of surface active agents in detergency. Above about 1315°C thermal decomposition of sodium sulphate becomes significant, according to Conroy. The products of the decomposition (Na, SO_2 and O_2) are soluble in the glass melt and are transferred across the interfaces between undecomposed sulphate liquid and the glass. This transfer of material upsets the interfacial tension between the two liquid phases resulting in development of a vigorous convective motion at all interfaces. Thus in this

temperature range a second function develops which produces a significant mixing effect in the glass. At about 1455°C Conroy believes that the partial pressure of the decomposition products of sodium sulphate reaches atmospheric pressure, (evidence produced later in this work may cast doubt upon this figure) and a new generation of bubbles develops in the glass. It is then proposed that these bubbles, by virtue of equilibria discussed below, serve a homogenising function in that they transfer soda equivalent (sodium and oxygen) from areas initially high in this component to the melt surface where the final dissolution of silica scum has produced relatively low soda concentration with respect to silica.

When a bubble develops containing gaseous decomposition products of sodium sulphate it contains sodium monoxide and sulphur trioxide equivalents in some proportion related to the composition of the glass in which the bubble formed. Equilibria are maintained in a three phase system: (i) the glass surrounding the bubble; (ii) molten sodium sulphate ("gall") as droplets in the bubble or as a thin film between bubble and glass; (iii) gas phase. This may be expressed

$$\text{Glass } (Na_2O,\ SO_3) \rightleftharpoons \text{Gall } (Na_2SO_4) \rightleftharpoons \text{Gas } (Na,\ SO_2 \text{ and } O_2).$$

When a bubble encounters glass rich in Na_2O, the glass-gall equilibrium is forced to the right as is the gall-gas equilibrium and the bubble will expand. Where silica rich glass is encountered the glass-gall equilibrium moves to the left as does the gall-gas equilibrium and the bubble shrinks. The intermediate sodium sulphate phase controls this three-fold equilibrium since the transported materials must pass through the gall layer. Further, Conroy maintains that the rates at which the reactions proceed to maintain the equilibria are extremely rapid.

If a melt is cooled to below the decomposition temperature liquid sodium sulphate forms but, since transfer of sodium sulphate into the glass demands decomposition as a prerequisite, the sodium sulphate solidifies as a separate phase. However, so long as the temperature of the melt is above 1455°C and some undecomposed sodium sulphate persists, then all three sulphate functions (wetting, stirring and soda transfer) operate simultaneously, and melting is completed sooner than with sulphate-free batch. Buss found that the smallest proportion of sulphate to produce effects that were still clearly visible in the minature melts of his hot stage microscope

experiments was 3%.

These then are the reasons for introducing sodium sulphate into the glass batch; the reason for investigating this compound may now be educed. It has been observed that large areas of the fire brick within the regenerator towers connected with the glass furnaces have been completely corroded away, and also that a large quantity of sodium sulphate has been found in the towers. How the sulphate reaches the regenerator is not clear. It may be physically blown in by the surface heating of a glass batch or it may have vaporised in the furnace and recondensed in the regenerator. In the latter case it would be interesting to determine the components of the vapour above sodium sulphate at various temperatures and also their absolute amounts.

Of the limited number of methods available for the determination of low vapour pressures at high temperatures two were adopted, the Knudsen effusion and torsion effusion techniques.

The Knudsen effusion method.[3,4,5] (please see footnote)

The sample under examination is contained in a small, usually cylindrical, container, completely sealed except for a small hole punched in the lid through which vapour effuses. The loss in weight of the cell due to this effusion is measured and used, as described below, to determine the vapour pressure.

It can be shown by elementary kinetic theory that the number of molecules striking unit surface area in unit time is given by

$$n = {}^{1}/_{4}\ P\bar{c}/kT$$

$$\text{where}\quad \bar{c} = (8RT/\pi M)^{\frac{1}{2}}$$

With pressure P_1 on one side of the hole and P_2 on the other, the rate of transfer is

$$\vec{n} - \overleftarrow{n} = {}^{1}/_{4}(P_1 c/kT - P_2 c/kT)$$

or if $P_2 = 0$

$$n = {}^{1}/_{4}\ P_1 \bar{c}/kT$$

Footnote

In the discussion of the two theoretical methods used the notation is that used in the original literature.

By converting to mass and substituting

$$m = nM/N$$

$$m = {}^{1}/_{4}\ PM/NkT.\ (8RT/\pi M)^{\frac{1}{2}}$$

$$m = P(M/2\pi RT)^{\frac{1}{2}}$$

$$P = m(2\pi RT/M)^{\frac{1}{2}}$$

The vapour pressure in atmospheres becomes

$$P_m = Z(MT)^{\frac{1}{2}}/44.33Bt \qquad (i)$$

where Z is the number of moles of material lost in an effusion run of t seconds through an orifice of area B.

Equation (i) is the ideal Knudsen equation which assumes that neither the hole nor the body of the cell exerts an influence on the effusing molecules. However any effusion orifice of finite length, that is every practical arrangement, will exert a chanelling effect on the vapour. This is accounted for by introducing a further factor into equation (i) thus,

$$P_m = Z(MT)^{\frac{1}{2}}/44.33W_BBt$$

where W_B is the Clausing factor[6] - the fraction of the gas molecules entering the hole which really comes through. A more complete discussion of the Clausing factor will be

undertaken later.

Whitman[7] was the first to take into account the influence of the main body of the cell. However his procedure involving infinite series leaves a solution which is rather inconvenient for practical application. A more simple method of approach by Motzfeld[8] leads to a solution of more practical use. This method will be considered.

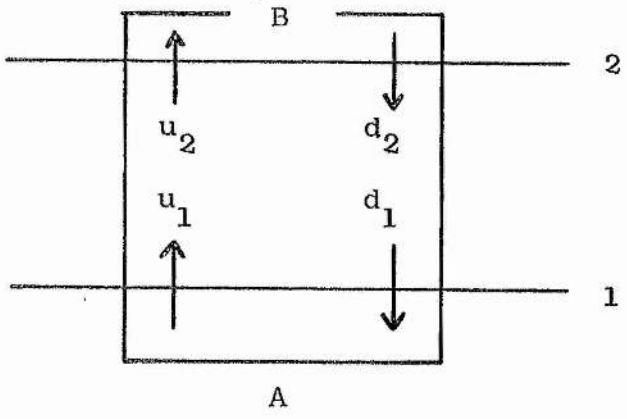


Fig. 1

In the diagram plane 1 is close to the evaporating surface and plane 2 is close to the lid. The pressures in these two planes will be considered.

At steady state with no hole the pressure will be evenly distributed. With a finite hole size this will no

longer be the case. The upward pressure u will be different from the downward pressure d for each plane and the pressure will be different in each plane. Here it is necessary to introduce another factor, to be considered in detail later, the coefficient of evaporation or condensation a.

A number of equations may now be derived. The rate of evaporation, which is proportional to aP_{eq}, is equal to the rate of recondensation plus the rate of escape through the hole,

$$aP_{eq} = ad_1 + fu_2$$

where $f = W_B B/A$ and A is the evaporating surface area. The upward pressure u_1 is made up of the evaporation from the surface plus the rebouncing of molecules coming from above.

$$u_1 = aP_{eq} + (1-a)d_1$$

The downward pressure at plane 2 is due to reflection of the upward molecules minus the fraction which escapes.

$$d_2 = (1-f)u_2$$

The upward pressure u_2 is due to the fraction W_A of the molecules heading upwards from the bottom plus the fraction $(1-W_A)$ of the molecules heading downwards from the top because this fraction is reflected upward again by the walls of the cell.

$$u_2 = W_A u_1 + (1- W_A)d_2$$

This is the first time we have met W_A, the fraction of the molecules leaving the bottom of the cell which arrives at the top. The pressure u_2 is equal to the measured pressure p_m and is therefore known. The solution of the above four equations is

$$P_{eq} = (1 + f(1/a + 1/W_A - 2))P_m \qquad \text{(ii)}$$

In this derivation some assumptions have been made which are not strictly valid. Pressures across any one plane were considered uniform and scattering at the wall giving rise to factor W_A has been assumed random.

In the limit $f \longrightarrow 0$ $P_{eq} \longrightarrow P_m$ and if $f = 1 = W_A = W_B$ $P_{eq} = P_m/a$ the equation for evaporation from a free surface. Equation (ii) may be rearranged to

$$P_m = P_{eq} - (1/a + 1/W_A - 2)P_m f$$

and plotting P_m against $P_m f$ gives a straight line of slope $-(1/a + 1/W_A - 2)$ and intercept P_{eq}, the equilibrium vapour pressure.

Apropos of the assumptions mentioned above some work by Ozhegov and Evseev[9] may be mentioned. These authors consider a cylindrical tube with a point source of molecular flux at its centre. The distribution of density of incidence of molecular flux on the wall of the tube having parameters, height H 9 cm and radius R 2.1 cm is shown in Fig. 2, and the distribution of density of incidence of molecular flux in the plane of circular cross section of a tube having the same parameters, in Fig. 3.

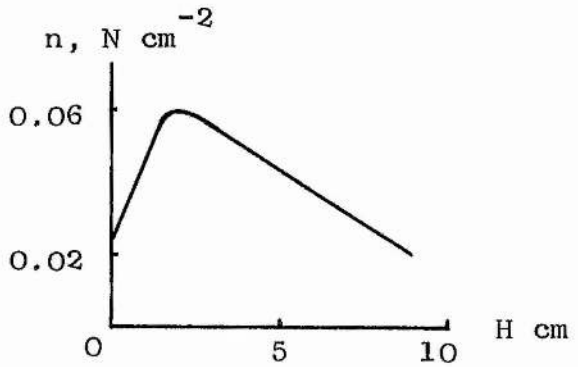


Fig. 2

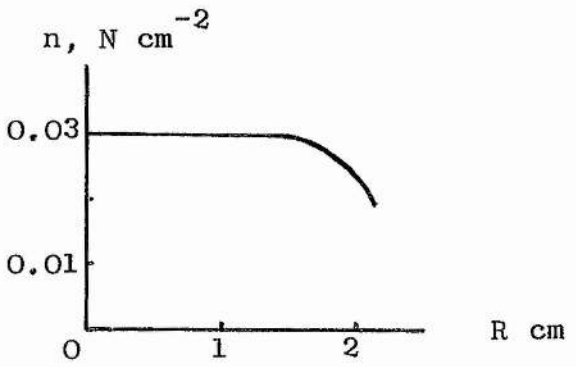


Fig. 3

Clausing[6] has derived correction factors which are

applicable to pressure determinations by the Knudsen method using an effusion orifice of finite length. However these factors cannot be used to calculate the pressure in a cell from the force exerted by vapour effusing from the cell, as in the torsion method to be considered later, because the force depends on the angular distribution of the effusing molecules as well as on their number. Freeman and Searcy[10] have used Clausing's equation for the angular distribution of effusing molecules to calculate suitable correction factors. A few are given below for purposes of comparison.

L/r	K	K'
0	1	1
0.2	0.9092	0.913
0.4	0.8341	0.831
0.6	0.7711	0.769

The values K were calculated by Clausing and values K' by Freeman and Searcy.

Balson[11] has mathematically computed what he terms

the chance of outflow W_o and compared his results to those derived by Whitman and Motzfeld. Using a cylindrical effusion vessel of radius 1 unit and length 2 units with a small axial effusion hole of radius r, his results for W_o are

Hole radius, r	0.1	0.2	0.3	0.5
W_o (Balson)	0.99530	0.97040	0.93480	0.83546
W_o (Whitman and Motzfeld)	0.9906	0.9635	0.9215	0.8083

Further mathematical analysis by Adams et al.[12] leads these authors to the conclusion that whereas at very low pressures, such that the Knudsen number (ratio of mean free path to orifice diameter) exceeds the limits for molecular flow, the Clausing theory is expected to be valid, the Clausing angular number distribution is not quantitatively correct for either the long or short orifices at low angles. They find that the Clausing theory predicts a greater probability of effusion in the forward direction than is found experimentally and recommend that when using the Knudsen method for vapour pressure measurements the orifices approximate to ideal i.e. they are as short as possible, when the angular

number distributions agree with theory. Monte Carlo computer methods have been applied to the case of effusion probabilities and related problems by Ward[13]. He states that "because the Monte Carlo method requires no mathematical approximations or simplyfying assumptions, results analogous to real cell behaviour are to be expected "and concludes that a comparison of these results with the Motzfeld treatment shows that Motzfeld's formula is applicable and quite accurate over a wide range of experimentally encountered conditions. Furthermore Ward's work shows that the upper limit of the Knudsen region is of the order of several tenths of a torr. Then gaseous collisions become important. Clausing's results are quite satisfactory if the length to radius ratio for the orifice is less than one.

Lozgachev[14] takes the problem from first principles and develops a general relation giving the conductance, to use his term, of a vessel with respect to vapour species. (See his equation 5). He then uses this general formula to calculate the conductance, or Clausing coefficient K, of a tube of circular cross section. The result he achieves is

$$K = 1/(1 + \ell/2r)$$

where ℓ is the tube length and r its radius. This result is interesting because it has also been put forward empirically by Kennard[15] who sets the limits of its application at $0 \leqslant \ell/r \leqslant 1.5$. This method of calculating the Clausing factor is adopted in this work.

What at first sight appears to be a straightforward method for the determination of absolute vapour pressures is now seen to be problematical. In the words of a French reviewer[16] "en réalité plusieurs difficultés théoriques et pratiques intimement liées viennent compliquer le problème". The next difficulty to be considered is that posed by the evaporation coefficient.

This quantity is defined by Burns[17] as the ratio of the rate of evaporation per unit area of a single vapour species from a surface to the equilibrium rate of flow of that species from the surface, both by evaporation and by reflection. Rosenblatt[18] opines that the vaporisation coefficient is the ratio of the number of molecules actually evaporating from a plane surface in unit time to the number of molecules calculated to strike that surface in unit time when the surface is in equilibrium with its vapour. The

vaporisation coefficient is closely related to the condensation coefficient which is the fraction of molecules striking a plane surface which sticks to the surface. The vaporisation and condensation coefficients are frequently assumed to be equal. It would seem imperative then that the nature of the evaporating surface of the sample should not be changed by condensation upon it of residual gases within the apparatus, since such condensation may cause reflection of vapour molecules by molecules of residual gas. This situation would change the evaporation coefficient. Nesmeyanov[19], however, is of the opinion that in the measurement of low pressures condensation of the residual gases on the surface is insignificant, and the measured pressure can be even lower than the residual pressure. The physical state of the surface is also a cause for concern as vaporisation will undoubtedly occur in the interstices between small crystals and contribute to the measured flux, giving, according to Rosenblatt and Lee[20], a higher vaporisation rate than that calculated from the exposed area, when the vaporisation coefficient is less than unity. Vidale[21] approaches the

vaporisation of a uniform porous powder sample by considering the problem to be one of diffusion through the powder. His treatment leads to the equation

$$A' = 1.55B(\epsilon/\alpha)^{\frac{1}{2}}$$

where A' is the effective vaporising area of the powder, B is the cross sectional area of the container, ϵ is the ratio of pore volume to total volume of powder and α is the vaporisation coefficient from a uniform plane surface which since

$$\alpha A' = \alpha_{powder} B \text{ gives}$$

$$\alpha_{powder} = 1.55(\epsilon\alpha)^{\frac{1}{2}}$$

The effect of the vaporisation coefficient on the equilibrium vapour pressure may be considered by the following treatment. Let S be the area of evaporation of the sample placed in the closed cell and α its evaporation (condensation) coefficient. Per unit time there will accumulate within the enclosure $n' \alpha S$ molecules where n' is the number of molecules colliding with the surface (per unit time and surface area). This gives a true pressure

P'. Now if the same enclosure is opened, then where there was previously equality of rate of evaporation and rate of condensation, there is now imbalance. The material balance may be written, where a is the area of the hole

$$na = n'\alpha S - n\alpha S$$

(i) (ii) (iii)

(i) rate of flow out

(ii) amount of evaporation

(iii) amount of condensation

$$n/n' = \alpha/(a/S + \alpha)$$

That is $P/P' = \alpha/(a/S + \alpha)$ where P is the equilibrium vapour pressure. Thus when a/S is small with respect to α, the measured pressure is essentially equal to the equilibrium pressure. However, as will be seen later, when α is very small, as not infrequently occurs, this is far from being the case. The question of the size of the vaporisation coefficient has been discussed by Brewer and Kane[22]. They find that virtually all materials that have been investigated have unit vaporisation coefficient and all ionic salts, such as the alkali halides, that vaporise

predominantly to a monomeric gaseous molecule are believed to have vaporisation coefficients close to unity. Some clearly demonstrated examples of low vaporisation coefficients occur when the main molecular gaseous species does not occur as such in the condensed phase. "In general", these authors conclude "we would expect low vaporisation coefficients when the main gaseous species is a polyatomic molecule that does not exist as such in the condensed phase and, because of the rigidity of the lattice, cannot readily form within the lattice". Motzfeld[8] attributes the low vaporisation coefficient of liquid sodium carbonate to the difficulty of bending the triangular carbonate ion to form the linear carbon dioxide molecule..

Determination of the vaporisation coefficient usually begins with the equation, by Motzfeld[8],

$$P_{eq}/P_m = 1 + f/\alpha$$

The equilibrium vapour pressure, P_{eq}, may be estimated by plotting the observed steady state pressure, P_m, as a function of the orifice area and extrapolating to zero orifice area.

Some examples of compounds whose vaporisation coefficients differ from unity are given below, together with the source of information.

Strontium chloride	0.3	[23]
Al_2O_3, Ga_2O_3, In_2O_3	0.3	[17]
Antimony	0.54	[20]
Graphite	0.15	[24]
Sodium hydrogenfluoride	0.006	[25]
Magnesium hydroxide	0.0018	[26]
Barium fluoride	0.9 ± 0.1	[27]

Taking the evaporation coefficient into account Balson[11] now computes a new overall chance of outflow $W_{o,\alpha}$ where $W_{o,\alpha}/W_o$ is given by

$$W_{o,\alpha}/W_o = \alpha/[1 - G(1 - \alpha)]$$

G is a dimension factor. $W_{o,\alpha} \longrightarrow W_o$ as $G \longrightarrow 1$ and becomes independent of α. With the effusion vessel filled completely up to the effusion hole the value of $W_{o,\alpha}/W_o$ becomes equal to α, for G is zero, and the evaporation coefficient is exerting its maximum effect. Thus a vessel should not

be filled to assist in the saturation of vapour inside. A few examples of Balson's results of calculations of the influence of the evaporation coefficient on the effusion rate from a cylindrical container with a small effusion hole are given. (Container radius R = 1, length L = 2; effusion hole radius r.)

Evaporation coefficient	$W_{o,\alpha}/W_o$ r/R = 0.1		$W_{o,\alpha}/W_o$ r/R = 0.2	
	Balson	Motzfeld	Balson	Motzfeld
0.9	0.9996	0.9990	Q.9948	0.9960
0.5	0.9968	0.9900	0.9552	0.9625
0.1	0.9720	0.9095	0.7031	0.7425
0.01	0.7463	0.5050	0.1767	0.2076

It will be noticed that during the calculation of vapour pressure from the Knudsen formula a value must be assumed for the molecular weight of the effusate. If the vapour species is identical with the condensed species no difficulty attaches to this; if, however, the two states cannot be accurately represented by the same molecular weight,

as for instance is the case for complete or partial dissociation in the vapour phase, then an allowance must be made. This question has been examined in some detail by Pashinkin[28,29,30] in a series of papers.

From the principal relationship defining molecular conditions of evaporation where the rate of evaporation is given by

$$p(2\pi RTM)^{-\frac{1}{2}} \text{ mol } s^{-1} \qquad \text{(iii)}$$

it follows that, in the effusion of two kinds of molecules the relationship between the numbers of molecules which have effused will be given by

$$n_1/n_2 = n_1^* \sqrt{M_2} \ /n_2^* \sqrt{M_1} \qquad \text{(iv)}$$

where n_1 and n_2, n_1^* and n_2^* are the numbers of molecules of each kind respectively outside and inside the chamber. In the general case

$$A_xB_y(\text{solid}) \rightleftharpoons {}^{x}/_{z}\, A_z\ (\text{gas}) + {}^{y}/_{v}\, B_v\ (\text{gas}) \qquad \text{(v)}$$

the relationship between the numbers of molecules of components A_z and B_v is

$$n_{A_z}/n_{B_v} = xv/zy.\sqrt{M_{B_v}/M_{A_z}} \qquad \text{(vi)}$$

The total weight of substance evaporated is

$$m = m_{A_z} + m_{B_v} \qquad \text{(vii)}$$

Replacing numbers of molecules in (vi) by numbers of moles m_{A_z}/M_{A_z} and m_{B_v}/M_{B_v} we find,

$$m_{A_z}/m_{B_v} = xv/zy \cdot \sqrt{M_{A_z}/M_{B_v}} \qquad \text{(viii)}$$

A combination of (vii) and (viii) yields

$$m_{A_z} = \frac{m \frac{xv}{zy} \sqrt{\frac{M_{A_z}}{M_{B_v}}}}{1 + \frac{xv}{zy} \sqrt{\frac{M_{A_z}}{M_{B_v}}}} \qquad \text{(ix)}$$

and

$$m_{B_v} = \frac{m}{1 + \frac{xv}{zy} \sqrt{\frac{M_{A_z}}{M_{B_v}}}} \qquad \text{(x)}$$

The total vapour pressure P_{tot} is given by,

$$P_{tot} = P_{A_z} + P_{B_v} \qquad \text{(xi)}$$

Writing the formula for calculating the vapour pressure by the Knudsen method in the form

$$P = cm/\sqrt{M} \qquad \text{(xii)}$$

we find

$$P_{A_z} = cm_{A_z}/\sqrt{M_{A_z}} \qquad \text{(xiii)}$$

and

$$P_{B_v} = cm_{B_v}/\sqrt{M_{B_v}} \qquad \text{(xiv)}$$

The nominal vapour pressure, calculated on the assumption that no dissociation occurs is then

$$P_{nom} = cm/\sqrt{M_{A_x B_y}} \qquad \text{(xv)}$$

Substituting (ix) and (x) in (xiii) and (xiv) respectively we obtain,

$$P_{A_z} = \frac{c\,\frac{xv}{zy}\,m}{\sqrt{M_{B_v}} + \frac{xv}{zy}\sqrt{M_{A_z}}} \qquad \text{(xvi)}$$

$$P_{B_v} = \frac{cm}{\sqrt{M_{B_v}} + \frac{xv}{zy}\sqrt{M_{A_z}}} \qquad \text{(xvii)}$$

From (xi), (xv) and (xvi) we obtain

$$P_{tot} = \frac{(1 + \frac{xv}{zy})\ cm}{\sqrt{M_{B_v}} + \frac{xv}{zy}\sqrt{M_{A_z}}} \qquad \text{(xviii)}$$

Dividing (xviii), (xvi) and (xvii) respectively by (xv) we obtain the conversion formulae for calculating the total and partial pressure of the components of the nominal vapour pressure in measurements by the Knudsen method

$$P_{tot} = KP_{nom} = \frac{(1 + \frac{xv}{zy})\sqrt{M_{A_x B_y}}}{\sqrt{M_{B_v}} + \frac{xv}{zy}\sqrt{M_{A_z}}} \cdot P_{nom} \qquad \text{(xix)}$$

$$P_{A_z} = K_{A_z} P_{nom} = \frac{\frac{xv}{zy}\sqrt{M_{A_x B_y}}}{\sqrt{M_{B_v}} + \frac{xv}{zy}\sqrt{M_{A_z}}} \cdot P_{nom} \qquad \text{(xx)}$$

$$P_{B_v} = K_{B_v} P_{nom} = \frac{\sqrt{M_{A_x B_y}}}{\sqrt{M_{B_v}} + \frac{xv}{zy}\sqrt{M_{A_z}}} \cdot P_{nom} \qquad \text{(xxi)}$$

Pashinkin[29] goes on to discuss the calculation of vapour pressure in Knudsen experiments where there are more than two components in the gas phase, and finally[30] derives expressions for the factors, K above, in the

general case

$$K = \frac{P_{tot}}{P_{nom}} = \frac{\sqrt{M_A}\sum_{i=1}^{n} x_i}{\sum_{i=1}^{n}\left(x_i\sqrt{M_i}\right)} \qquad \text{(xxii)}$$

$$K_i = \frac{P_i}{P_{nom}} = \frac{x_i\sqrt{M_A}}{\sum_{i=1}^{n}\left(x_i\sqrt{M_i}\right)}$$

Where $\sum_{i=1}^{n} x_i$ is the sum of the stoichiometric coefficients on the right hand side of the equation for dissociative evaporation and x_i is the stoichiometric coefficient of the given component in the dissociative evaporation equation;

$$A(\text{solid}) \rightleftharpoons x_1B_1(\text{gas}) + x_2B_2(\text{gas}) + \ldots + x_nB_n(\text{gas}).$$

This brief general discussion on the Knudsen method should not be concluded without mention being made of the accuracy of the method in general terms. Rossman and Yarwood[31] derive an expression met with earlier that,

$$a/A = \alpha(P/p - 1)$$

in which a is the area of the effusion orifice, A is the effective evaporating area, p is the measured pressure and P the saturation vapour pressure. If $p = xP$, where x is very nearly equal to one, then

$$x = [1 + (a/A\alpha)]^{-1}$$

or putting $a/A = f$,

$$x = [1 + (f/\alpha)]^{-1} \qquad \text{(xxiv)}$$

With the orifice in the form of a short tube the resultant impedance to the flow of vapour will be equivalent to making the aperture area, a, smaller. The area of the actual surface can only be larger than A, the cross section area of the crucible. Thus, these authors maintain, (xxiv) gives the maximum possible error in the vapour pressure determination, the error being zero when $x = 1$. Since x is a function of a, A and α so the effective area of the condensate is fundamentally related to the pressure of the effusing gas. Whitman[32] takes this a stage further. He derives an expression analogous to that of Rossman and Yarwood,

$$p/P = K = 1/[1 + f/W_A - f] \quad (1 \geqslant W_A > 0) \qquad \text{(xxv)}$$

for a cell with an infinitely thin orifice. The condensation coefficient, α, is unity and p is determined by the measured effusion rate. It is apparent from (xxv) that K will be greater than, equal to, or less than Rossman and Yarwood's x, depending on the depth of the cell which determines W_A (see Motzfeld's notation[8]). The effusion rate is therefore not only dependent on how much effective area of condensate is present but also on where it is located relative to the orifice. This, Whitman concludes, would prove a pertinent consideration for any experimental arrangement and hence, in general, the assumption of a steady state pressure is not justifiable. Rossman and Yarwood's x would not therefore be a particularly reliable estimate of the accuracy of an effusion measurement. Komlev[33] derives an equation relating the saturated vapour pressure, P_p and the pressure measured at the exit of the effusion orifice, P_e, which, he claims, is satisfied with any effusion chamber.

$$P_p = P_e \left(\frac{1}{k_o} + \frac{a(1 - k\alpha)}{A\alpha k}\right)$$

Where k and k_o are the Clausing coefficients for chamber and orifice respectively. From mathematical considerations

Muradov[34] finds that the total amount of vapour flowing from the chamber when the aperture is fairly small should be virtually independent of α, and further, that Knudsen's method in its classical form can be applied both when the mean free path, $\lambda >> \Lambda$ and when $\lambda << \Lambda$. (Here Λ is a dimension factor given by $\Lambda^2 = [H^2 + (2r_o)^2]$ where H is the height and $2r_o$ the diameter of the effusion chamber.) This means that the effusion method can be used to measure vapour pressures, however small, provided that there is no reverse flow of vapour from the receiver, through the aperture, into the chamber.

During the course of this summary of the Knudsen method for the measurement of vapour pressures an attempt has been made to introduce the concepts of Clausing factors and coefficients of evaporation and condensation. Mention has also been made of the complications arising out of vapour phase dissociation and finally the idea of the accuracy of the method, as the ratio of measured vapour pressure to saturated vapour pressure, has been touched upon. The weight loss method has many of these points in common with the second method used, the torsion method now to be introduced.

The Torsion effusion method[35]

This is a modification of the Knudsen method but it deserves separate treatment since it allows the measurement of vapour pressure without involving an assumed value of the molecular weight in the calculation. It tends therefore to take on considerable importance.

The Knudsen vessel is pierced by two effusion orifices, eccentric and symmetrical with respect to the axis of a torsion fibre by which it is suspended. The pressure of the vapour jets causes a couple which is balanced by the restoring couple of the torsion fibre. This torque F resulting from the effusion of vapour from a cell through holes of area a_1 and a_2 at distances q_1 and q_2 from the axis of suspension of the cell is determined from the angle ϕ through which the torque twists the fine wire of torsion constant D by which the cell is suspended. The torque is related to ϕ and to the pressure P_T in the cell by

$$F = D\phi = (q_1 a_1 + q_2 a_2) f P_T / 2$$

The factor f is the ratio of the force resulting from the effusion of vapour through a hole of finite length to the force expected if the hole had an infinitesimal length

(c.f.[10]). The torsion constant D is calculated from the period of oscillation t of the suspension system alone and the period t_w with a weight of known moment of inertia I added

$$D = 4\pi^2 I/(t_w^2 - t^2).$$

Since no value need be assumed for the molecular weight in deriving the vapour pressure by this method, it is theoretically possible to determine an accurate value for the molecular weight of the vapour species by using this and the Knudsen weight loss method in combination. If the results of the simultaneous vapour pressure determinations disagree by more than experimental error, the molecular weight, M, assumed in the weight loss calculation, and therefore the vapour pressure calculated from it, P_k, is incorrect. Since P_k is inversely proportional to the square root of the value assumed for M, the correct value for the molecular weight, M^*, of the effusing vapour is related to the actual pressure P_T by

$$M^* = M(P_k/P_T)^2.$$

If more than one species is effusing M^* is related to the molecular weights of the effusing species by

$$M^* = 1/(m_1 M_1^{-\frac{1}{2}} + m_2 M_2^{-\frac{1}{2}} + \ldots + m_n M_n^{-\frac{1}{2}})^2$$

where m_n is the mass fraction and M_n the molecular weight of the nth species.

Some practical points bearing on the method may now be mentioned. McCreary and Thorn in a series of experiments on nickel di-halides[36] and zinc and cadmium[37] found that the vapour pressure determined by torsion exceeded that calculated from weight loss measurements and they believe that this disagreement reveals a real systematic difference between the two procedures. "We surmise", these authors conclude, "that the principal source of the difference is to be found in the effusate which returns preferentially to the same side of the cell from which it originated. Such imparts an additional torque and thereby yields a total torque which is too large. At least one can state that such a correction must now be evaluated before correct measurements of the pressure can be obtained from the torsional recoil".

Balson[38] investigated the effect of small residual pressures of air on the recoil force. He found that between 10^{-5} and 10^{-3} torr air pressure the recoil force was undiminished, but at pressures above 10^{-3} torr it decreased gradually. He concluded that complete de-gassing of the substance is not quite so important in this method.

Juey Hong Rai and Gregory[39] make mention of the uncertainty in locating the centre of gravity of the cell. They preferred to use calibration constants based on the vapour pressure of a standard substance e.g. silver, rather than those based on moment of inertia measurements. This enabled them to include the Clausing-Freeman-Searcy orifice correction in the experimentally derived cell-torsion constant.

Searcy and Freeman[40] estimate the maximum error in the torsion pressure determinations to be 18%. They consider all errors in both methods of determination to be less than 2% except for the errors in the torsion constant D and in the angle of rotation. The torsion constant varied for these authors by as much as 10% during the course of a series of runs and the accuracy with which the null point can be located was not greater than 7% of a typical deflection.

An estimation of an error of 15% for a combination of torsion and weight loss methods is quoted by Lindscheid and Lange[41].

This concludes the introduction to the methods that have been used in this work for the investigation of vapour pressures of salts at elevated temperatures. Although interest was centred primarily upon sodium sulphate the other alkali metal sulphates were investigated for comparative purposes, together with magnesium and calcium sulphates, sodium metasilicate and sodium peroxide. Sodium sulphate has attracted a good deal of endeavour in the past, potassium sulphate rather less and the other compounds mentioned above, little or none. A review of the literature dealing with the vapour pressures of these compounds now follows. Each compound is dealt with in turn as far as possible although, inevitably, overlapping does occur.

Sodium sulphate.

An early study of the thermal decomposition of sodium sulphate was undertaken by Mlle. Marchal[42]. This lady heated sodium sulphate in a platinum crucible and followed the progress of the decomposition by observing the weight loss of the crucible. The decomposition rate was reported

as being very slow at 1300°C. The heating time and weight loss figures are reproduced below.

T°C	Heating time, hrs.	wt. loss %
1300	1	0.87
	+ 1	2.61
	+ 63 minutes	3.78
	+ 1	4.23

Only weight loss measurements are recorded and no vapour pressure or decomposition pressure measurements are reported at all, which calls in question the results attributed to Marchal appearing in Kroger and Stratmann's paper, page 317 figure 9[43].

This author does report that the weight losses were considerably increased by addition of silica and aluminium oxide to the sodium sulphate.

Terres[44] does give the values of the dissociation pressure over sodium sulphate as 1.3×10^{-2} atmospheres at 1350°C and 0.7×10^{-2} atmospheres at 1200°C, but unfortunately does not record any experimental details.

However an effect similar to that observed by Marchal is recorded. The partial pressure of sulphur trioxide rises if silica is mixed with sodium sulphate. Although no explanation is offered this rise would seem to be due to a reduction in activity of sodium monoxide as it reacts with silica, resulting in a shift in the equilibrium

$$Na_2SO_4 \rightleftharpoons Na_2O + SO_3$$

to the right.

Quantitatively the effects are reported as follows, ½ mole % SiO_2 raises the partial pressure of SO_3 from 10 to 150 torr, 1 mole % SiO_2 gives 200 torr
2 mole % SiO_2 give 400 torr, all at 1350°C.
Similar effects are stated as resulting from additions of aluminium oxide and ferric oxide.

Liander and Olsson[45] measured the vapour pressure of sodium sulphate by drawing a current of air over a heated sample. Their results are expressed by the relation

$$\log_{10} (P/\text{torr}) = -\frac{7230\ K}{T} + 4.42$$

The temperatures at which they worked ranged between 1100°C and 1450°C.

The results of an investigation by Eyber[46] give the following values for the variation of the vapour pressure of sodium sulphate with temperature.

$T^{o}C$	vapour pressure/atmospheres
1000	0.02
1100	0.06
1200	0.17
1300	0.37
1400	0.80

He gives a value for the heat of vaporisation as 40.4 k cal mol^{-1} (168.9 kJ mol^{-1}) and also quotes Lorenz and Herz[47] as giving the boiling point of sodium sulphate as 1702 K. This author also estimates the value of the equilibrium constant

$$Kp = \frac{pNa_2O.pSO_3}{pNa_2SO_4}$$

$T^{o}C$	log (Kp/atm)
1000	-14.3
1100	-12.6
1200	-11.1
1300	-10.0
1400	-8.8
1500	-7.4

In 1961 Kroger and Stratmann[43] reported, with full experimental details, on their experiments with sodium sulphate.

These authors heated sodium sulphate in a nickel Knudsen cell over a temperature range of 752°C to 851°C which is below the melting point of sodium sulphate at 884°C. An aluminium foil plate suspended over the cell from the arm of the microbalance collected the condensate which was shown to be almost exclusively sodium sulphate. Their apparatus was very sensitive, the limit of measurement being within the range of 2×10^{-5} up to 10^{-1} torr for values of vapour pressure.

The values they measured for the vapour pressure of sodium sulphate are given below.

T°C	vapour pressure/torr
752	0.103×10^{-3} 0.145×10^{-3}
783	0.425×10^{-3}
814	1.25×10^{-3} 0.62×10^{-3}
836	1.9×10^{-3}
841	2.7×10^{-3}
851	3.85×10^{-3}

They found the heat of vaporisation to be 79 k cal mol^{-1} (330.2 kJ mol^{-1}). The vapour pressure equation they give is

$$\log[p(vap)/torr] = -1.73 \times 10^4 K/T + 13.1$$

and extrapolation from this yields a boiling point of 1700 K.

For their work on potassium sulphate these authors used both nickel and platinum cells and the vapour pressure results obtained differed markedly. A selection is given:

Nickel		Platinum	
T^oC	vapour pressure, torr	T^oC	vapour pressure, torr.
857	0.45×10^{-3}	841	0.67×10^{-3}
925	1.5×10^{-3}	917	2.6×10^{-3}
961	2.3×10^{-3}	951	4.9×10^{-3}
999	6.8×10^{-3}	999	12.3×10^{-3}

This difference is probably due, although these authors do not explain it, to the attack of the nickel by potassium sulphate. One might conclude that the true value for the vapour pressure of sodium sulphate could also be higher than the one quoted due to attack of the nickel cell.

A liquid is mentioned comprising alkali sulphate and oxide at temperatures below the melting point, suggesting a eutectic, but the amount of oxide formed is stated as being negligible.

During the course of a study of the behaviour of glass melts with salts, Bruckner[48] used an entrainment method to determine the partial pressures resulting from the action of high temperature on sodium sulphate. He showed, prior to the major experiments, that platinum has no decomposing effect on sodium sulphate. The atmospheres used in the experiments were, nitrogen, air, oxygen, and an $SO_2 + \frac{1}{2}O_2$ mixture. The loss in weight of the sodium sulphate sample was measured at various temperatures and at various carrier gas flow rates and Bruckner reached the conclusion that "... from these measurements only the decomposition pressure and not the vapour pressure can be determined." This is rather misleading since reference to the final column in his Table 5 shows weight losses resulting from sodium sulphate being heated under an atmosphere of $SO_2 + \frac{1}{2}O_2$ and there would seem to be a large enough partial pressure of SO_3 to inhibit decomposition of the sodium sulphate while allowing it to evaporate.

At 1300°C the weight loss was too small to detect (see final column, Bruckner's Table 5), indicating a very low vapour pressure. However, by applying the formula quoted by Bruckner (equation 2 page 97) to the values given in Table 5 for 1400°C (final column) the following results for the vapour pressure of sodium sulphate are obtained,

$$15.97 \times 10^{-6} \text{ atm.}$$

$$7.90 \times 10^{-6}$$

$$5.00 \times 10^{-6}$$

$$4.57 \times 10^{-6}$$

giving a mean value of 8.36×10^{-6} atm or 6.35×10^{-3} torr.

The author goes on to describe extrapolation of his weight loss measurements to a flow speed of zero "where equilibrium partial pressure exists." If this statement were true the values in the nitrogen and air columns of Table 5 would give the values in the last column when extrapolated back to zero flowrate. This does not seem to be the case; the decomposition effect does not appear to be eliminated, thus the above statement must be called in question. The extrapolated measurements will give the decomposition sulphur trioxide pressure together

with a vapour pressure of sodium sulphate and sodium monoxide.

The curve in his figure 5 shows that a decomposition pressure of one atmosphere is reached at approximately 1850°C and the author states that no boiling was observed up to 1750°C.

Bruckner also investigated the dependence of weight loss on the partial pressure of water vapour in damp nitrogen atmospheres. He found, (see his Table 6 and figure 4) a linear dependence of the weight loss on the square root of the water vapour partial pressure. This may be due to

$$Na_2SO_4 = Na_2O + SO_3 \qquad \text{(xxvi)}$$

$$Na_2O + H_2O = 2NaOH \qquad \text{(xxvii)}$$

The sodium hydroxide is more volatile than sodium oxide and would cause an increased weight loss.

For reaction (xxvii) we have

$$K = [NaOH]^2/[Na_2O][H_2O]$$

and, since $[Na_2O]$ will be constant due to the equilibrium set up in reaction (xxvi), $[NaOH]^2 \propto [H_2O]$. Thus if the weight loss is proportional to the amount of sodium hydroxide present $[NaOH] \propto (pH_2O)^{\frac{1}{2}}$ [49].

The Russian authors Fotiev and Slobodin[50] heated sodium sulphate in a platinum vessel in an electric furnace. Dry air passed through the system at 0.1 litre per minute and was analysed for sulphur trioxide and sulphur dioxide. The residue was analysed for sulphate and alkali metal.

In a separate series of experiments samples of sodium sulphate were heated in a vacuum furnace at 2×10^{-5} mm Hg. The results showed that the change in weight of sodium sulphate after being heated from three to five hours up to 1390°C was not accompanied by the liberation of sulphur dioxide or sulphur trioxide and sodium oxide was not found in the solid phase.

Thus, these authors conclude, the loss in weight of sodium sulphate is due to volatilisation and not thermal dissociation. They found that the dependence of the amount of volatilisation on the duration of heating is almost linear, and the apparent activation energy of volatilisation they have calculated to be 77 kcal mol^{-1} (322 kJ mol^{-1}). Sodium sulphate was found to volatilise at an appreciable rate only above 1200°C in air.

Volatilisation from 1 cm^2 surface area of the melt in one hour, in mole % Na_2SO_4, was measured as

0.36×10^{-4} at 1100°C

0.24×10^{-3} at 1200

0.18×10^{-2} at 1320

0.48×10^{-2} at 1390.

However in a vacuum at 1050°C the volatilisation was found to be considerable,

12.3% after 15 min

49.0% after 40 min

80.8% after 70 min

86.1% after 80 min

When sodium sulphate was heated in crucibles of quartz, porcelain, corundum or alundum a considerable change in weight occurred, accompanied by the liberation of sulphur dioxide.

These authors conclude that sodium sulphate undergoes almost no dissociation up to 1400°C at atmospheric pressure or in a vacuum and that loss in weight of sodium sulphate in platinum is due to volatilisation, but in other materials chemical reaction with them is possible.

Holmquist[51] considered the primary thermal reactions

above the melting point

$$Na_2SO_4(l) = Na_2O(l) + SO_3(g)$$

$$SO_3(g) = SO_2(g) + \tfrac{1}{2}O_2(g)$$

$$Na_2SO_4(l) = Na_2O(l) + SO_2(g) + \tfrac{1}{2}O_2(g)$$

$$Na_2O(l) = 2Na(g) + \tfrac{1}{2}O_2(g)$$

and for pure sodium sulphate of unit activity derived

$$K_3 = [Na_2O].pSO_2.pO_2^{\frac{1}{2}} = K_1.K_2 = [Na_2O].pSO_3.K_2 \quad \text{(xxviii)}$$

From this the activity of sodium oxide, $[Na_2O]$, is inversely proportional to the partial pressure of sulphur trioxide. Thus the decomposition pressure of sodium sulphate would approach infinity at zero activity of sodium oxide. The partial pressure of sodium oxide or its equivalent above molten sodium sulphate must be directly proportional to the activity of this oxide in the melt, which is a function of the gas composition above the melt. It might seem that the activity of sodium oxide would become high in a melt subjected to an atmosphere free of sulphur dioxide and oxygen. Holmquist considered that this condition would obtain at the very surface only.

Holmquist has extrapolated from the data of Kellogg[52] and tabulates values for log K_3 which may be plotted

against temperature according to the equation

$$\log K = 11.9 - 3.38 \times 10^4 \, K/T$$

T/K	Log K_2	Log K_1	log K_3
1157	0.40	-17.73	-17.3
1200	0.56	-16.85	-16.3
1300	0.87	-14.90	-14.0
1400	1.13	-13.35	-12.2
1473			-11.0
1500	1.35	-12.00	-10.6
1600	1.54	-10.75	-9.2
1700	1.71	-9.67	-8.0

Holmquist goes on to discuss a suggestion by Manring et al.[53] that sodium sulphate decomposes according to the reaction

$$Na_2SO_4(l) = 2Na(g) + SO_2(g) + O_2(g)$$

(since Brewer and Margrave[54] have shown that alkali metal oxides do not exist in the vapour phase), and that the total pressure reaches one atmosphere at 1425°C. At this temperature, Holmquist points out, from equation (xxviii) and using values from the table above, $\log[Na_2O] = -7.1$ when $pSO_2 = pO_2 = \frac{1}{4}$. Thus the partial pressure of sodium

oxide is negligible and the above reaction insignificant with regard to material transport.

Wyatt[55] has indicated that calculations based on the reaction

$$Na_2SO_4 = 2Na(g) + SO_2(g) + O_2(g)$$

reveal that $\Delta G^o/T = 60.39$ cal deg^{-1} (252.43 J deg^{-1}) at 1600 K and 24.90 cal deg^{-1} (104.08 J deg^{-1}) at 2000 K hence $pNa^2.pSO_2.pO_2 \backsim 5 \times 10^{-14}$ atm^4 at 1600 K and $\backsim 3.5 \times 10^{-6}$ atm^4 at 2000 K.

With evaporation into a vacuum this would give a total vapour pressure of $\backsim 10^{-3}$ atmospheres at 1600 K and $\backsim 10^{-1}$ atmospheres at 2000 K.

The same author introduced the idea of a correlation between the stabilities of the alkali oxides towards formation of metal vapour and the relative stabilities of sodium and potassium sulphates. In support the following calculations were given,

$$Na_2O(l) \longrightarrow 2Na(g) + \tfrac{1}{2}O_2(g)$$

$\Delta G^o/T = 20$ cal deg^{-1} (83.6 J deg^{-1}) at 1600 K

$= 3.55$ cal deg^{-1} (14.84 J deg^{-1}) at 2000 K

$pNa^2.pO_2^{\frac{1}{2}} = 4 \times 10^{-5}$ atm $^{5}/2$ at 1600 K

$= 0.13$ atm $^{5}/2$ at 2000 K

and $K_2O(l) \rightarrow 2K(g) + \frac{1}{2}O_2(g)$

$\Delta G^{\circ}/T = 5.26$ cal deg^{-1} (21.99 J deg^{-1}) at 1600 K

with $pK^2.pO_2^{\frac{1}{2}} = 0.07$ atm $^{5}/2$ at 1600 K.

A mass spectrometric method has been adopted by Ficalora et al.[56]. These authors heated sodium sulphate in an alumina lined Knudsen cell and analysed the effusing beam with a mass spectrometer. Above sodium sulphate the ions observed were Na^+, O_2^+, SO_2^+, SO_3^+, SO^+ and S^+. No change was experienced when the temperature was raised to 40°C above the melting point. Ionisation efficiency curves indicate that Na^+, O_2^+, SO_2^+ and SO_3^+ over solid sodium sulphate are parent ions whereas SO^+ and S^+ are formed by fragmentation.

The authors conclude that the vaporisation of sodium sulphate is properly described by the reaction

$$Na_2SO_4(s) = 2Na(g) + SO_2(g) + O_2(g)$$

and $$SO_2(g) + \frac{1}{2}O_2(g) = SO_3(g)$$

From their results Ficalora et al. were able to calculate

the heat of decomposition of solid sodium sulphate as ΔH^{o} = 315 ± 13 k cal mol^{-1} (1316 kJ mol^{-1}) at 1087 K which compares well with the calculated value of ΔH^{o} = 317 ± 3 kcal mol^{-1} (1325 kJ mol^{-1}) at 1087 K.

Potassium sulphate

This compound has not been quite so extensively studied as the sodium salt but a review of the main sources follows. Kroger's work[43] has already been mentioned in connection with the choice of crucible materials. Nettleton and Raask[57] examined the rate of evaporation of potassium sulphate droplets in oxidising, neutral and reducing atmospheres; they attribute the much greater rate of weight loss in a reducing atmosphere, hydrogen or carbon monoxide, to the reduction of potassium sulphate on the surface of the drop with the production of more volatile products. They give the following values for the vapour pressure of potassium sulphate.

Temp/K	Vapour pressure/torr
1400	0.05
1600	0.65
1800	6.8

Kosugi[58] measured the vapour pressure and dissociation pressure of potassium sulphate. His plot of log p against 1/T reveals a break in linearity near to 1555 K with the slope of the line becoming steeper on the high temperature side. The low temperature slope Kosugi assumes to be proportional to the heat of vaporisation of potassium sulphate to potassium sulphate molecules in the vapour phase, and the appearance of a break and a steeper slope he attributes to a remarkable change in the form of the evaporating molecules. This change he interprets as thermal dissociation. He used the Knudsen effusion method and found that the saturated vapour pressure was given by

$$\log(P/\text{torr}) = -1.253 \times 10^4 \text{ K/T} + 7.724$$

with an average heat of vaporisation of 57.3 ± 8.6 kcal mol^{-1} (239.5 kJ mol^{-1}) in the experimental temperature range up to 1500 K. The relation of dissociation pressure to temperature was

$$\log(P/\text{torr}) = -3.275 \times 10^4 \text{K/T} + 20.83$$

and the heat of dissociation in the temperature range above 1500 K was 150 ± 22,5 kcal mol^{-1} (627 kJ mol^{-1}).

Ficalora and co-workers[56], using the same practical arrangement as for sodium sulphate, claim that some degree of vaporisation to monomeric molecules takes place with potassium sulphate. The mass spectrometric examination revealed the presence of K_2SO_4 molecules in the vapour phase where no Na_2SO_4 molecules had been found. The heat of sublimation is given by these authors as 72,8 ± 2,0 kcal mol^{-1} (304,3 kJ mol^{-1}) and the heat of decomposition of solid potassium sulphate they found to be 364 ± 11 kcal mol^{-1} (1521 kJ mol^{-1}) at 1158 K compared to the calculated value of 352,0 ± 3,0 kcal mol^{-1} (1471 kJ mol^{-1})

Halstead[59] measured the saturated vapour pressure of potassium sulphate by a combination of the Knudsen effusion and transpiration techniques and found that the vapour pressure may be expressed by the equation

$$\log_{10}(P/atm) = -1.47 \pm 0.09 \times 10^4 K/T + 6.84 \pm 0.69$$

between 1190 and 1342 K (the melting point of potassium sulphate). The mean heat of sublimation was found to be 67.3 ± 4.0 kcal mol^{-1} (281.3 kJ mol^{-1}) over this range of temperature. Dubois and Millet[60], using the transpiration technique, measured the heat of vapourisation as 61,8 kcal mol^{-1} (258,3 kJ mol^{-1}).

Lithium, Rubidium and Caesium Sulphates.

Jaeger[61] mentions that lithium sulphate decomposes at 1200°C and that vaporisation of caesium sulphate is first noticeable at 1325°C. Hopkin[62] compares the volatilities of potassium, rubidium and caesium sulphates and finds they are in the ratio of 1:1.4:2.1. Hopkin supposes that the volatility may be determined by the changes of bonding which take place in the liquid state rather than by the ionic bonding in the solid state. The stronger the bonding in the solid state the more it appears to give rise to a weaker bonding when liquid.

Spitsyn and Shostak[63] studied the volatilities of all the normal sulphates of the alkali metals. The sulphates were heated in air, in a current of air and in a current of steam over a range of temperature from 800° to 1200°C, and the results may be interpreted in terms of evaporation to the molecular sulphate for potassium, rubidium and caesium, but for lithium and sodium sulphates decomposition occurred. The volatility of lithium sulphate, these authors conclude, is related to the polarising action of the lithium ion upon the sulphate ion and the corresponding reduction of the ionic nature of the bond between them. Sodium sulphate is the least volatile of the alkali metal sulphates,

perhaps because the polarising action of the sodium ion upon the sulphate ion is considerably less than that of the lithium ion, and the polarisability of the sodium ion by the sulphate ion is less than that for the ions of potassium, rubidium and caesium. No conclusions are reached concerning the absolute values of the vapour pressures of the sulphates investigated.

The mass spectrometric work of Ficalora et al[56] has already been mentioned in connection with the sulphates of potassium and sodium. They found nothing to indicate the presence of lithium sulphate or lithium monoxide in the vapour phase, but they did find evidence for the existence of rubidium and caesium sulphates as gaseous molecules. The heat of decomposition of solid lithium sulphate is given as 324 $\pm$ 12 kcal mol^{-1} (1354 kJ mol^{-1}) at 1080 K. The heats of sublimation for rubidium and caesium sulphates are quoted as 69.7 $\pm$ 1.0 kcal mol^{-1} (291.3 kJ mol^{-1}) and 63.9 $\pm$ 1.7 kcal mol^{-1} (267.1 kJ mol^{-1}) respectively. A plot of log P against 1/T is shown for potassium, rubidium and caesium sulphates.

Apropos of the question of the existance of the monoxides of alkali metals in the vapour phase, Brewer and Margrave[54] consider it extremely unlikely except possibly in the case of lithium monoxide.

Magnesium and calcium sulphates.

Stern and Weise[64] list calculated equilibrium pressures for the dissociation of calcium sulphate and a sample of these is included below.

T/K	P/atm
500	1.97×10^{-25}
1000	3.73×10^{-8}
1200	2.29×10^{-5}

They do not give any pressures for magnesium sulphate. Both sulphates are assumed to decompose directly to the oxides. Dewing and Richardson[65] examined the decomposition equilibria for calcium and magnesium sulphates by differential thermal analysis. The following pressure values are taken from their graphs at the temperatures indicated

$CaSO_4$		$MgSO_4$	
$p.SO_2.p^{\frac{1}{2}}O_2/atm^{3/2}$	T/K	$p.SO_2.p^{\frac{1}{2}}O_2/atm^{3/2}$	T/K
10^{-4}	1470	10^{-3}	1180
10^{-3}	1560	10^{-2}	1260
		10^{-1}	1350

Knopf and Staude[76] interpret the results of their flow-type experiments on $MgSO_4$ in terms of the reaction

$$MgSO_4 \rightleftharpoons MgO + SO_3$$

They derive the relation

$$\log P/\text{torr} = -1.2487 \times 10^4 \, K/T + 11.3748$$

between vapour pressure and temperature.

Tschappat and Pièce[77] sum up their results on the decomposition

$$CaSO_4 \rightleftharpoons CaO + SO_2 + \tfrac{1}{2}O_2$$

by the equation

$$\log P/\text{torr} = -14024 \, K/T + 10.280$$

yielding a ΔH value of 404 kJ $mole^{-1}$ (96.2 k cal $mole^{-1}$). These authors find complete agreement between results from anhydrite and dehydrated gypsum, and Zawadski's[78] work on anhydrite. On the other hand Zawadski's results using dehydrated gypsum are very close to those of Marchal[79] with the same starting material and markedly different from Tschappat and Pièce. Marchal's results yield a ΔH value of 260 k J $mole^{-1}$ (62.2 k cal $mole^{-1}$).

The start of thermal decomposition of magnesium sulphate is variously reported as occurring at 895°C[66], 740-760°C[67] and above 1120°C[68]. During an investigation of the kinetics of thermal decomposition of magnesium sulphate, Kowalska[69] found the energy of activation, as he termed it, to be 49 358.3 cal mol^{-1} (206.5 kJ mol^{-1}) Cueilleron and Hartmanshenn[67] found calcium sulphate to be still undissociated at 970°C and Ostroff and Sanderson[66] consider that it begins to decompose at 1149°C.

Sodium metasilicate.

A literature search has revealed nothing whatever on the vapour pressure of this compound as such. However Kroger and Sörström[70], during work on silicate glasses, measured the vapour pressure of a glass of composition $Na_2O.SiO_2$: a few of their values are given below.

T°C	P $torr^{-1}$ x 10^4
1035	39
1061	75
1175	77
1200	94

They noted a break in the vapour pressure line at the melting

point and calculated the heat of dissociation as 105 kcal mol^{-1} (439 kJ mol^{-1}) for the process

$$Na_2SiO_3(solid) \longrightarrow Na_2O\ (vapour) + SiO_2\ (solid)$$

They consider that volatilisation is determined in this case by this dissociation process together with the accompanying one of

$$Na_2O \longrightarrow 2Na + \tfrac{1}{2}O_2$$

Sodium peroxide

Early workers on sodium peroxide considered it to begin to decompose at or about its melting point of 460°C[71] with a heat of dissociation of 37.7 kcal (157.6 kJ mol^{-1}). Tzentnershver and Blumenthal[72] state that the decomposition pressure reaches one atmosphere at 657°C, which they term the dissociation temperature. However, Rode and Gol'der[73] have found that sodium peroxide begins to decompose slowly at approximately 350°C, and at 545°C the evolution of oxygen becomes violent leaving only sodium monoxide. That sodium monoxide is the final product was noted by Brewer and Margrave[74] who used the fact to prepare small samples of the monoxide.

Experimental

1. Knudsen weight loss method

a. Apparatus

The three principal constituent parts of the experimental assembly are portrayed schematically in Figs. 4, 5, and 6. The vacuum system was simple and comprised essentially a mercury diffusion pump backed by a rotary oil pump. Two pressure gauges were incorporated as indicated; the Edwards Vacustat McLeod gauge was used as a rough indicator of the pressure and the Pirani gauge was brought into use as the pressure decreased towards its operational level. The trap shown as an adjunct of the Pirani gauge was only used to protect it from undesirable condensates during the initial heating of the furnace when the apparatus was first set up; it was not used during experimental observations. The furnace was attached to this vacuum line by a picened, metal to glass, cone and socket joint. The residual pressure within the furnace, using this system, decreased to about 2×10^{-5} torr.

The furnace was massively constructed in brass, circular in horizontal cross section. The heating current was led in through heavy, water-cooled, copper electrodes, insulated from the body of the furnace by ceramic lead throughs. The heating element, a cylinder of tungsten foil, was fixed between the two copper electrodes. Concentric with the heating element and with each other, three molybdenum heat

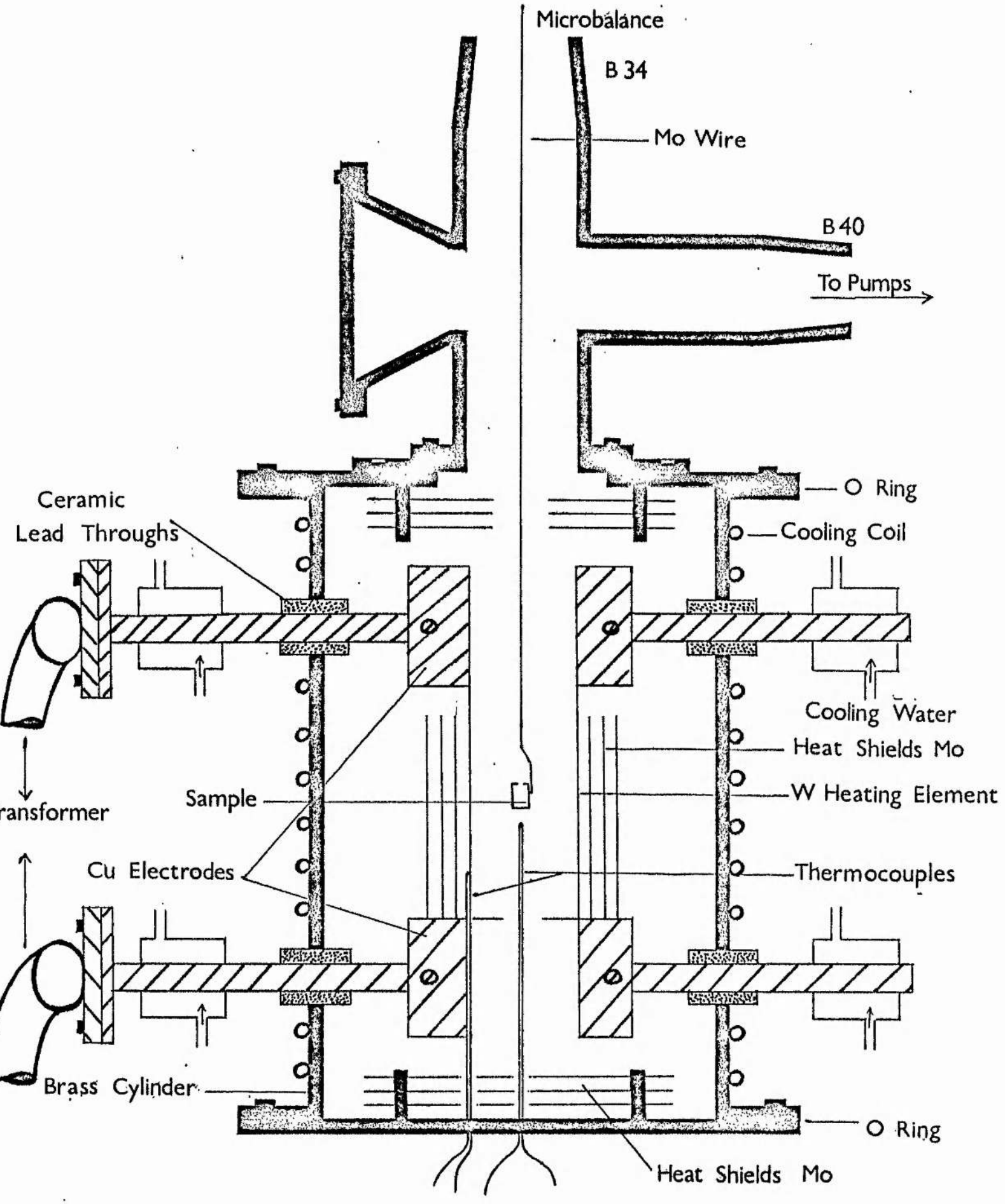


fig. 4. FURNACE

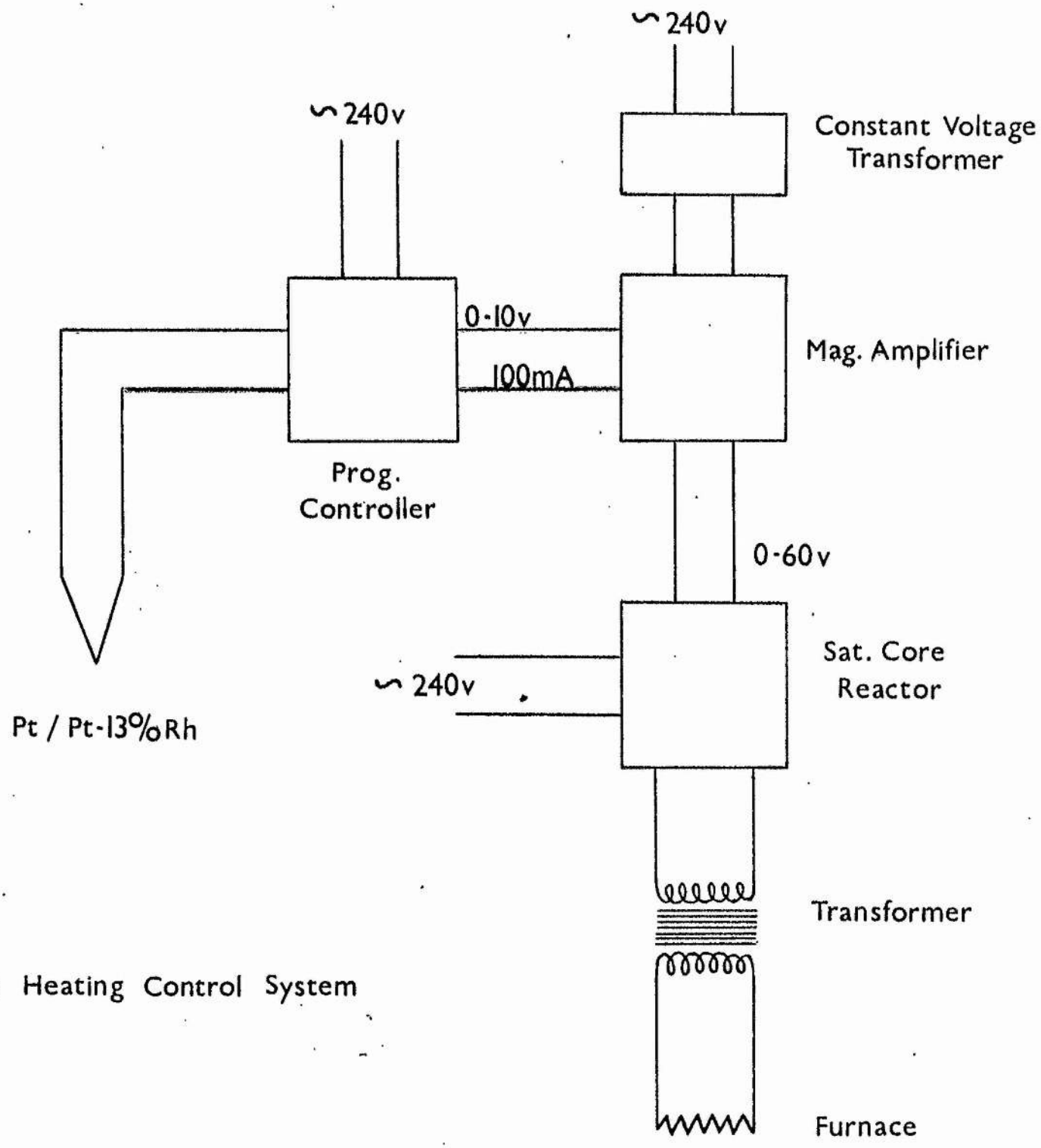


fig.5. Heating Control System

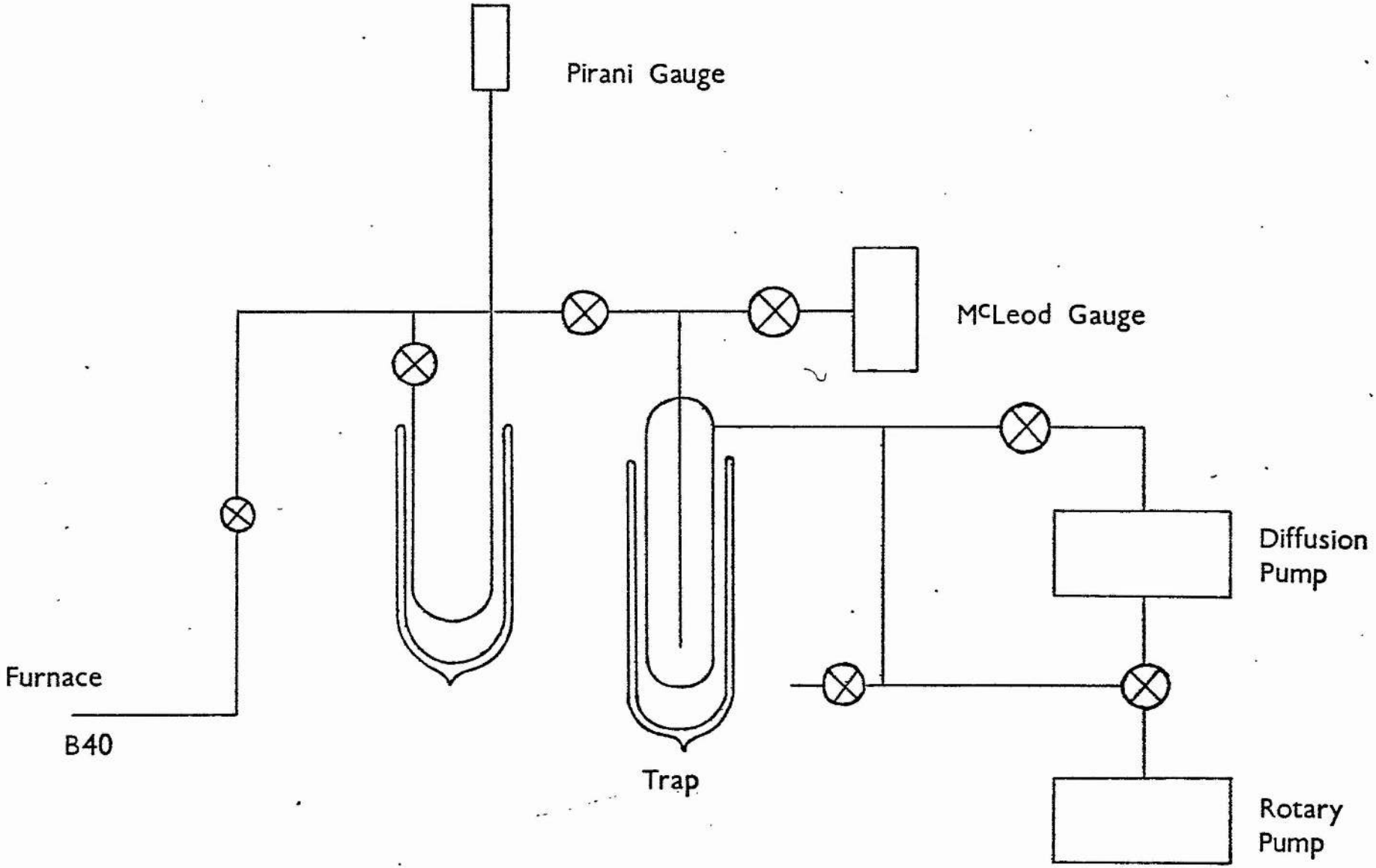


fig 6 The Vacuum System

shields rested on the bottom electrode but did not reach to the top electrode. Two sets of three circular molybdenum heat shields were disposed one each at the top and bottom of the body of the furnace. The thermocouples were led into the furnace through ceramic lead throughs. Both these thermocouples are of platinum and platinum - 13% rhodium, the one on the left in the diagram operates the temperature control system and is fixed close to the outside of the heating element.

The heating control system enabled the furnace temperature to be maintained to $\pm$ 3 K at 1200 K.

Experimental weight losses were measured on a vacuum microbalanc as supplied by C.I. Electronics. This balance was fixed on the top of the furnace via a B 34 cone and socket joint. The crucible containing the sample was suspended by 0.25 mm diameter molybdenum wire from one arm of the balance. The loss in weight was followed on the meter of the balance control box. The tip of the balance arm was more than fifty centimeters above the hot part of the furnace, sufficient distance to enable any effects of temperature to be neglected. The total load on the balance was kept below 1.5 g.

The samples were all contained in cells of 0.4 cm^2 cross-section and depth 0.8 cm, cut down from spinel crucibles (equimolar Al_2O_3 + MgO). Previous work[59] has shown that cells of this material are

both inert and non-porous to potassium sulphate, and this condition was assumed to obtain for the other substances examined. The cells were closed by lids of 0.025 mm thick platinum foil which were held to the cell walls by a series of individually tightened loops of 0.25 mm diameter molybdenum wire. The relative coefficients of linear expansion of the various components ensured that these bindings tightened as the temperature was increased.

The effusion orifices were made with hardened steel punches, and were clean edged and circular under the microscope. Their diameters were checked by a series of microscope measurements. In every case the ratio of the cross-sectional area of the cell to the orifice area exceeded 100 to 1.

The temperature of the cell was measured by a platinum and platinum - 13% rhodium thermocouple situated just below the cell. The relative position of the cell and the thermocouple was kept the same for all experimental runs and for the initial calibration procedure using potassium chloride[59,75]. The results for KCl were as follows:

T/K	rate of weight loss/mg min^{-1}	P/torr	orifice area /cm^2
1053	1.72	1.02	1.9×10^{-3}
1073	2.60	1.56	
1086	3.38	2.04	
1109	5.14	3.13	

These results indicate a dependence of vapour pressure on temperature expressed by the equation

$$\log_{10} P/\text{torr} = -1.01 \times 10^4 \, K/T + 9.61$$

which is in fair agreement with previously published data.

b. Procedure

A sample of the material under investigation was ground and dried for about twenty four hours at 110°C. With the exception of the samples of rubidium and caesium sulphate and sodium metasilicate all the materials examined were of "Analar" quality. A small quantity of this dried material was then weighed into a spinel crucible, the weight of which had previously been determined. Enough was used to cover the bottom of the crucible to the depth of about 1 mm. The cell was now sealed with the platinum foil lid, already furnished with an effusion orifice of known size, the lid being held secure by bindings of molybdenum wire. The molybdenum suspension wire was fixed, care being taken to ensure that the cell was vertically below the point of suspension on the balance arm. The length of this suspension wire was kept the same throughout the entire series of experiments.

With the cell suspended in position evacuation was begun.

The apparatus was left to pump down for about twenty four hours before the furnace was switched on, then for a further three to six hours with the furnace at 200-400^{o}C, the temperature depending on the substance under investigation. When the temperature was raised to the first desired working temperature, not always the lowest, the temperature was allowed to stabilise over a period of up to half an hour, and, when it was clear that the relationship between the weight loss of the cell and the time of heating was linear, measurement commenced. The time over which a weight loss was measured varied with the temperature and the substance under test, from four to six hours with sodium sulphate to a matter of minutes for sodium peroxide. At the end of this period the furnace was adjusted to the next desired temperature, the pause for equilibration was observed, and the procedure was repeated. Weight losses were measured both after increasing and decreasing the furance temperature. At no time during a series of measurements was the pressure in the furnace allowed up to atmospheric although the furnace was switched off between two distinct sets of measurements when night intervened.

The vapour pressures were calculated from the standard Knudsen effusion equation, derived in the introduction, using these measured weight losses. A Clausing correction factor was used

in each calculation to adjust for the channelling effect of the orifice upon the effusing molecules. (See introduction)

The Knudsen orifices used were of three different sizes, 0.0725, 0.0490 and 0.0336 cm diameter. The Clausing factor for each orifice was calculated using the rule derived by Kennard[15].

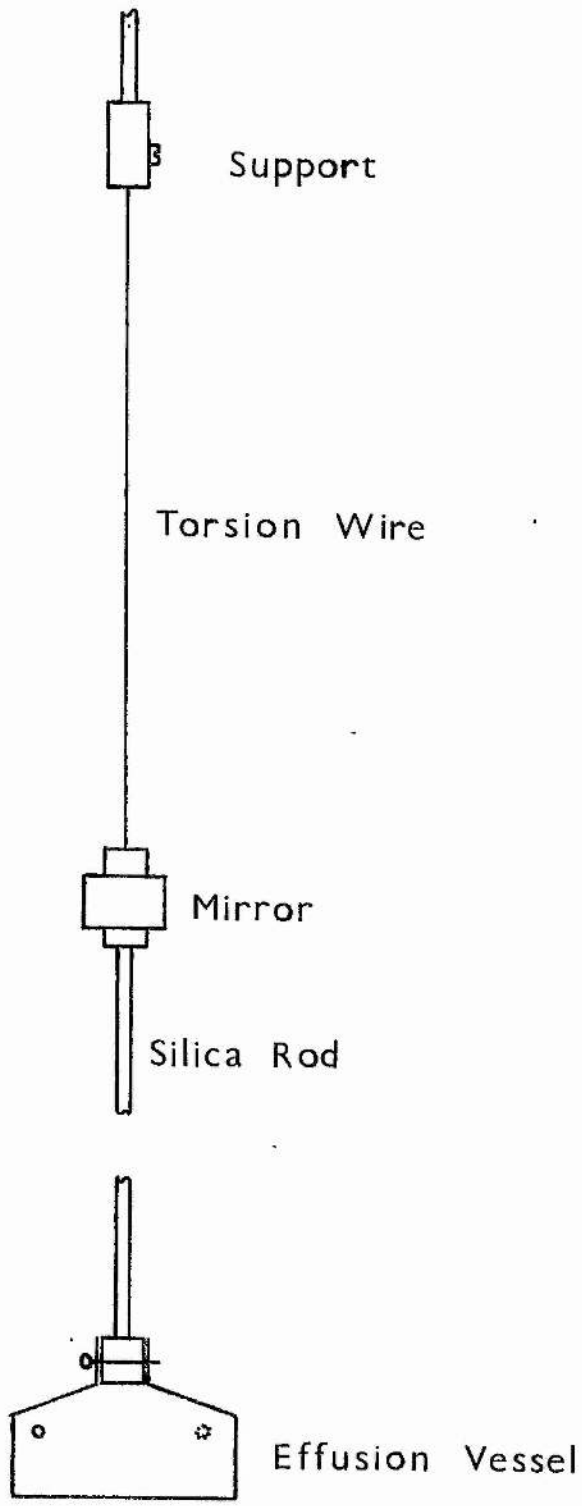
2. Torsion method

a. Apparatus

The vacuum system, furnace and heating control system used in this part of the experimental work were identical to those described in the previous section. The effusion cell itself and the arrangement of the torsion system are shown in Fig. 7. The cell was made of platinum of wall thickness 0.005" and carried two effusion orifices of 0.048 cm diameter symmetrically placed each side of the torsion axis. These holes were 1.10 cm apart. The torsion wire was about 30 cm of 0.0032" diameter steel wire, the mounting at the bottom of the wire carried a mirror reflecting light to a scale up to 1.5 meters away.

b. Procedure

The samples of each compound used were from the same source as



Torsion System

fig 7

those used in the weight loss experiments and they were treated in the same way, i.e. ground and dried at 110°C for about 24 hours prior to use. The equation relating the vapour pressure of the compound to the measureable parameters is

$$P = 2K\phi/(q_1a_1 + q_2a_2)$$

where q_1, q_2 are the distances of the orifices, areas a_1, a_2, from the torsion axis, ϕ is the angle through which the assembly is rotated and K is a constant. This constant was determined by carrying out experiments on potassium chloride, the vapour pressure of which is accurately known. By this method the constant K is made to incorporate the torsion constant of the wire and the Clausing coefficient of the orifices. This standardisation was repeated at the end of the torsion experiments but no change in K was observed.

A small amount of sample was put into the cell, the cell suspended in position and the furnace evacuated. The temperature was raised and at certain temperatures, after allowing time for equilibration, the deflection was measured. This process was repeated up the temperature scale and then down again; for each compound the cycle was repeated five or six times.

The furnace used in this series of experiments was designed and built to carry out weight loss experiments and this

imposed serious limitations on the measurements attempted by the torsion technique. As will be seen later, some compounds failed to give a measurable response and others required the position of the null point to be judged to distances of a millimetre or less; hence the large number of readings taken. Attempts to increase the size of the deflection by lengthening the torsion wire were frustrated by the increased effect of the unavoidable vibration, critical when such short distances are involved. Ideally the distances between the orifices and the axis should be greatly increased but this was impossible given the geometry of the furnace and heating element. However compounds with high enough vapour pressures gave encouraging results.

1. Alkali metal sulphates

Results of Knudsen effusion experiments

The results of the weight loss experiments on the alkali metal sulphates are given in Tables 1 to 5, and they are presented graphically in Figs. 8 to 12. In these figures $\log_{10}P'$ is plotted against 1/T, P' being the value of the vapour pressure calculated by using a vapour phase molecular weight corresponding to the species M_2SO_4 for each compound. For K_2SO_4, Rb_2SO_4 and Cs_2SO_4 the points may be represented by single straight lines within the experimental error. However Li_2SO_4 and, to a lesser extent, Na_2SO_4 show a distinct departure from rectilinearity. Both Li_2SO_4 and Na_2SO_4 melt within the temperature range of the experiment (the melting points are marked by vertical lines on the relevant graphs) but even when fusion occurs no very great change in the slope would be expected at the melting point, since the heat of fusion is only of the order of 24 kJ mol^{-1} and the slopes in the melting region are about 230 kJ mol^{-1}.

The results obtained for Na_2SO_4 and K_2SO_4 are compared with those of former investigators in Figs. 13 and 14. Because of the differences in interpretation of the vapour constitution, the mass-spectrometric results are not strictly comparable with the others until a mean molecular weight correction has been made to the latter. If, as seems likely at the higher temperatures at least,

Table 1

Lithium sulphate Li_2SO_4 (Molecular weight 110)

T/K	Rate of wt. loss /mg min^{-1}	P'/torr	orifice area/cm^2
1034	3.33×10^{-3}	7.37×10^{-4}	4.1×10^{-3}
1066	3.67×10^{-3}	8.23×10^{-4}	
1106	6.67×10^{-3}	1.52×10^{-3}	
1130	1.40×10^{-2}	3.24×10^{-3}	
1161	2.33×10^{-2}	5.47×10^{-3}	
1214	7.33×10^{-2}	1.76×10^{-2}	
873	8.33×10^{-4}	3.71×10^{-4}	1.9×10^{-3}
929	1.08×10^{-3}	4.97×10^{-4}	
986	1.40×10^{-3}	6.62×10^{-4}	
1034	2.00×10^{-3}	9.69×10^{-4}	
1082	3.42×10^{-3}	1.70×10^{-3}	
1126	5.50×10^{-3}	2.78×10^{-3}	
1176	2.15×10^{-2}	1.11×10^{-2}	

Fig. 8.

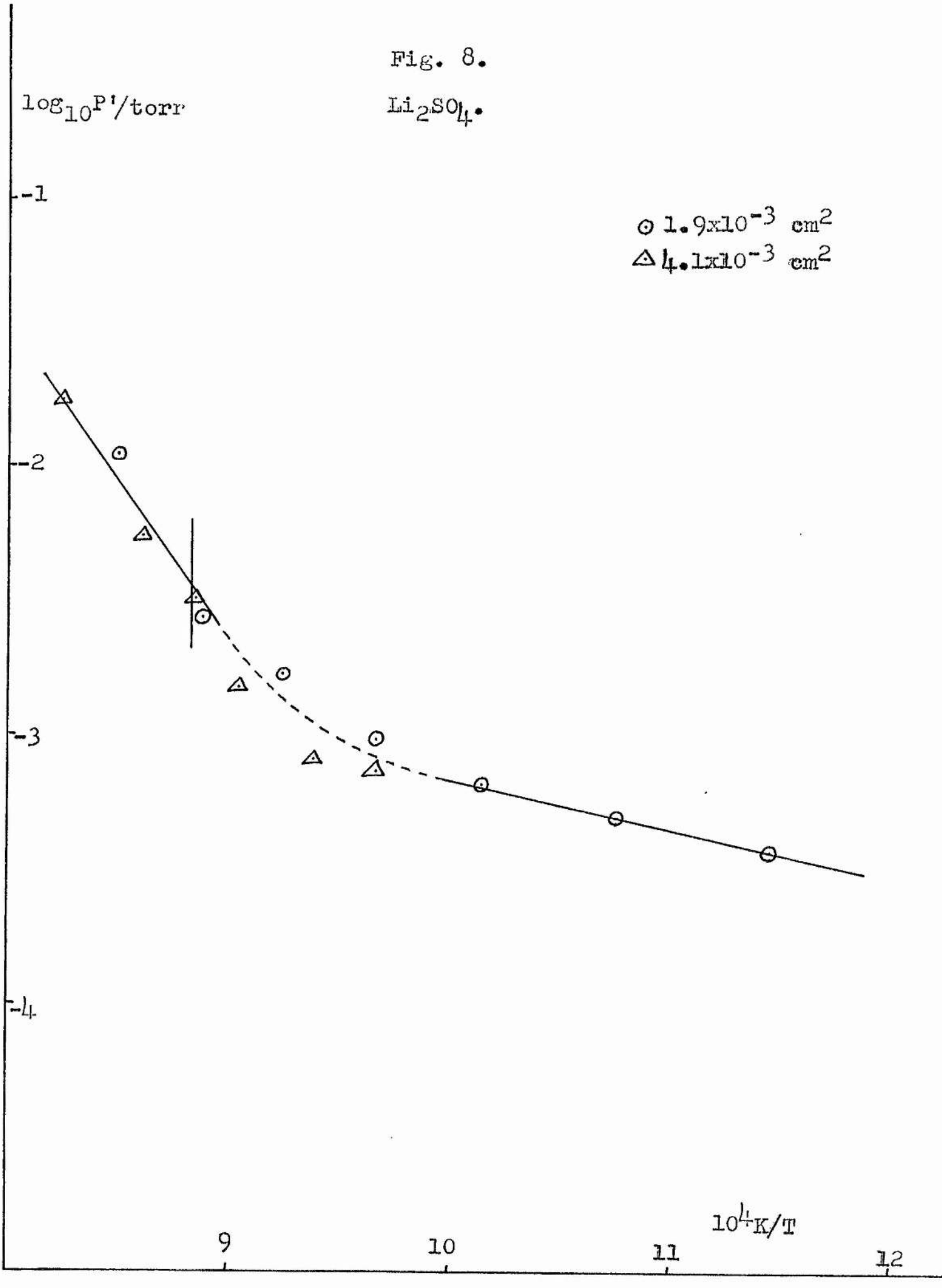

$\log_{10}P'/\text{torr}$
Li_2SO_4.
⊙ 1.9×10^{-3} cm^2
△ 4.1×10^{-3} cm^2
-1
-2
-3
-4
9
10
11
12
$10^4 K/T$

Table 2

Sodium sulphate Na_2SO_4 (Molecular weight 142)

T/K	Rate of wt. loss /mg min^{-1}	P'/torr	Orifice area/cm
848	9.01×10^{-5}	1.57×10^{-5}	4.1×10^{-3}
877	1.66×10^{-4}	2.95×10^{-5}	
886	1.39×10^{-4}	2.51×10^{-5}	
954	5.20×10^{-4}	9.70×10^{-5}	
1135	5.33×10^{-3}	1.09×10^{-3}	
931	1.33×10^{-4}	5.39×10^{-5}	1.9×10^{-3}
938	1.43×10^{-4}	5.80×10^{-5}	
990	3.33×10^{-4}	1.39×10^{-4}	
1050	5.33×10^{-4}	2.29×10^{-4}	
1099	1.25×10^{-3}	5.49×10^{-4}	
1151	2.67×10^{-3}	1.20×10^{-3}	
1199	9.62×10^{-3}	4.43×10^{-3}	
898	5.06×10^{-5}	4.40×10^{-5}	8.9×10^{-4}
987	1.87×10^{-4}	1.71×10^{-4}	
1049	2.58×10^{-4}	2.42×10^{-4}	
1123	1.42×10^{-3}	1.37×10^{-3}	
1164	2.66×10^{-3}	2.63×10^{-3}	
1200	4.89×10^{-3}	4.90×10^{-3}	

Fig. 9.

$\log_{10} P'/\text{torr}$ Na_2SO_4.

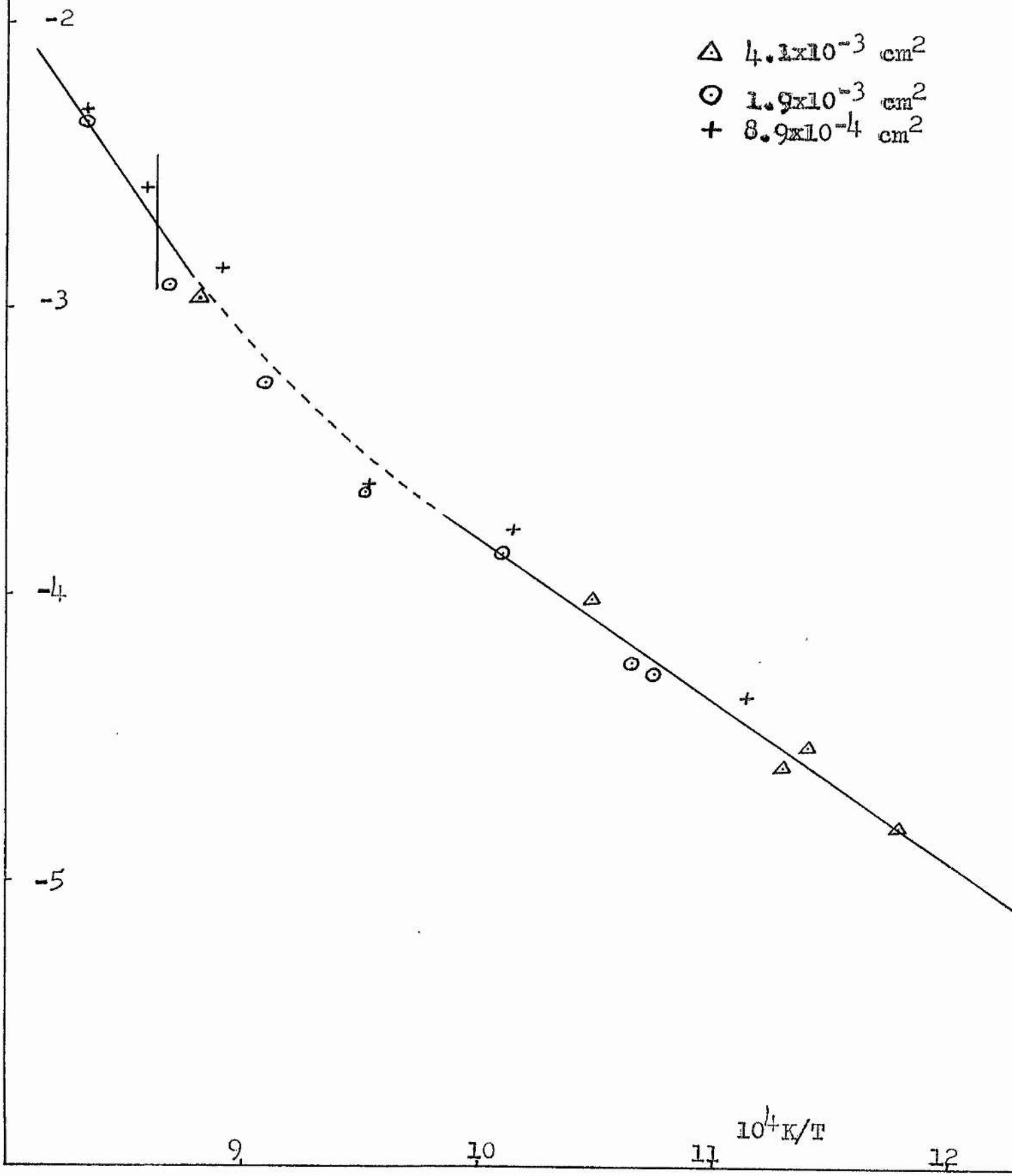


Table 3

Potassium sulphate K_2SO_4 (Molecular weight 174)

T/K	Rate of wt. loss /mg min^{-1}	P'/torr	Orifice area/cm^2
948	6.06×10^{-5}	2.24×10^{-5}	1.9×10^{-3}
1000	2.82×10^{-4}	1.07×10^{-4}	
1106	2.33×10^{-3}	9.30×10^{-4}	
1173	9.67×10^{-3}	3.97×10^{-3}	
1226	1.67×10^{-2}	6.99×10^{-3}	
1271	4.33×10^{-2}	1.85×10^{-2}	
1296	5.00×10^{-2}	2.16×10^{-2}	
1086	7.69×10^{-4}	6.63×10^{-4}	8.9×10^{-4}
1221	1.00×10^{-2}	9.14×10^{-3}	
1246	1.30×10^{-2}	1.20×10^{-2}	
1266	1.70×10^{-2}	1.58×10^{-2}	
1286	2.30×10^{-2}	2.16×10^{-2}	

Fig. 10.

K_2SO_4.

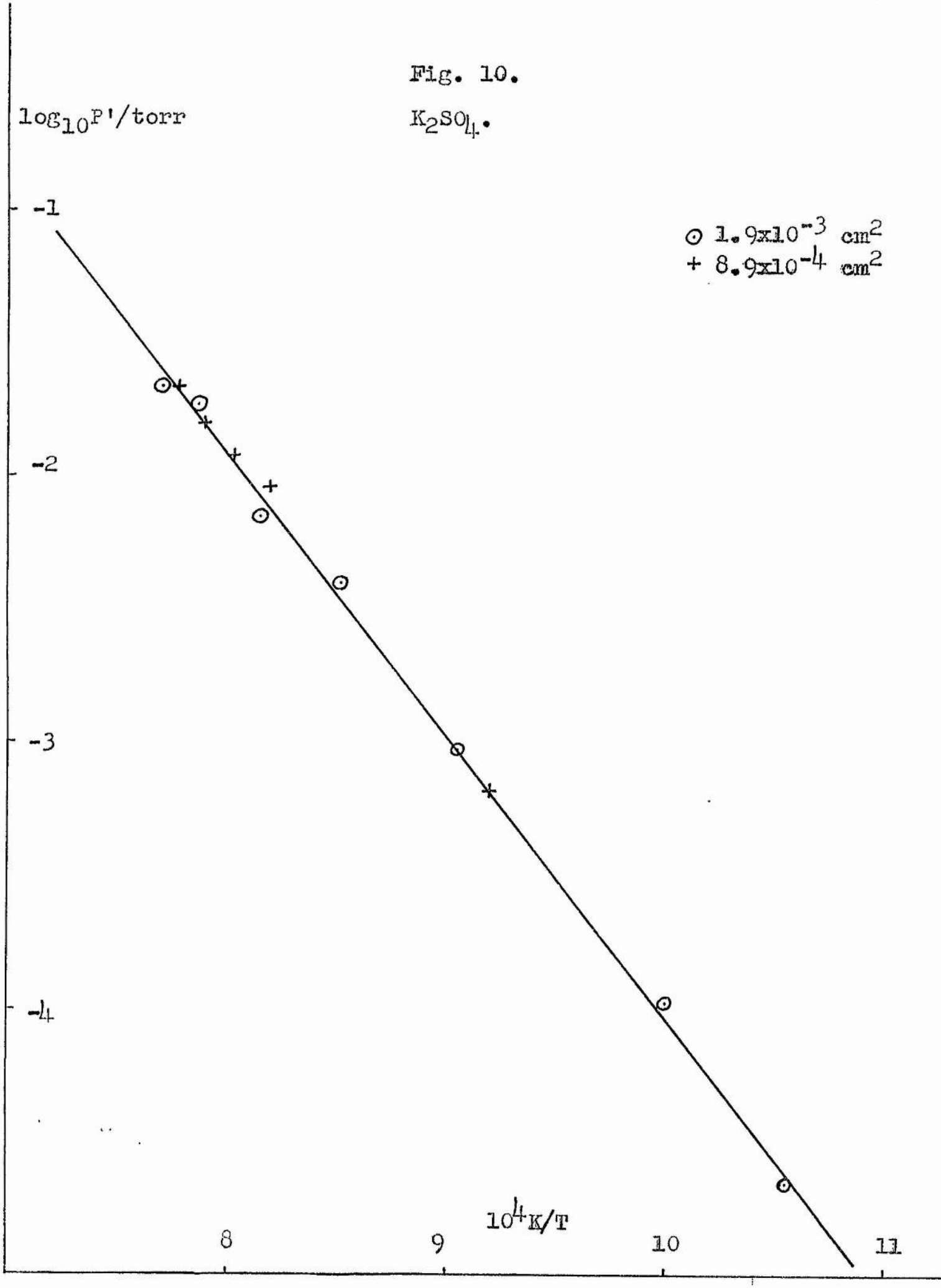


Table 4

Rubidium sulphate Rb_2SO_4 (Molecular weight 267.03)

T/K	Rate of wt. loss /mg min^{-1}	P'/torr	orifice area/cm
864	3.70×10^{-4}	4.80×10^{-5}	4.1×10^{-3}
898	1.41×10^{-3}	1.86×10^{-4}	
956	3.33×10^{-3}	4.55×10^{-4}	
1078	1.76×10^{-2}	2.55×10^{-3}	
1096	2.73×10^{-2}	4.00×10^{-3}	
1158	2.20×10^{-2}	3.30×10^{-3}	
1197	4.00×10^{-2}	6.11×10^{-3}	
1243	7.40×10^{-2}	1.15×10^{-2}	
1281	0.126	1.99×10^{-2}	
1111	6.95×10^{-3}	2.24×10^{-3}	1.9×10^{-3}
1138	1.60×10^{-2}	5.22×10^{-3}	
1181	2.20×10^{-2}	7.31×10^{-3}	
1265	6.20×10^{-2}	2.13×10^{-2}	
1220	2.80×10^{-2}	9.46×10^{-3}	

Fig. 11.

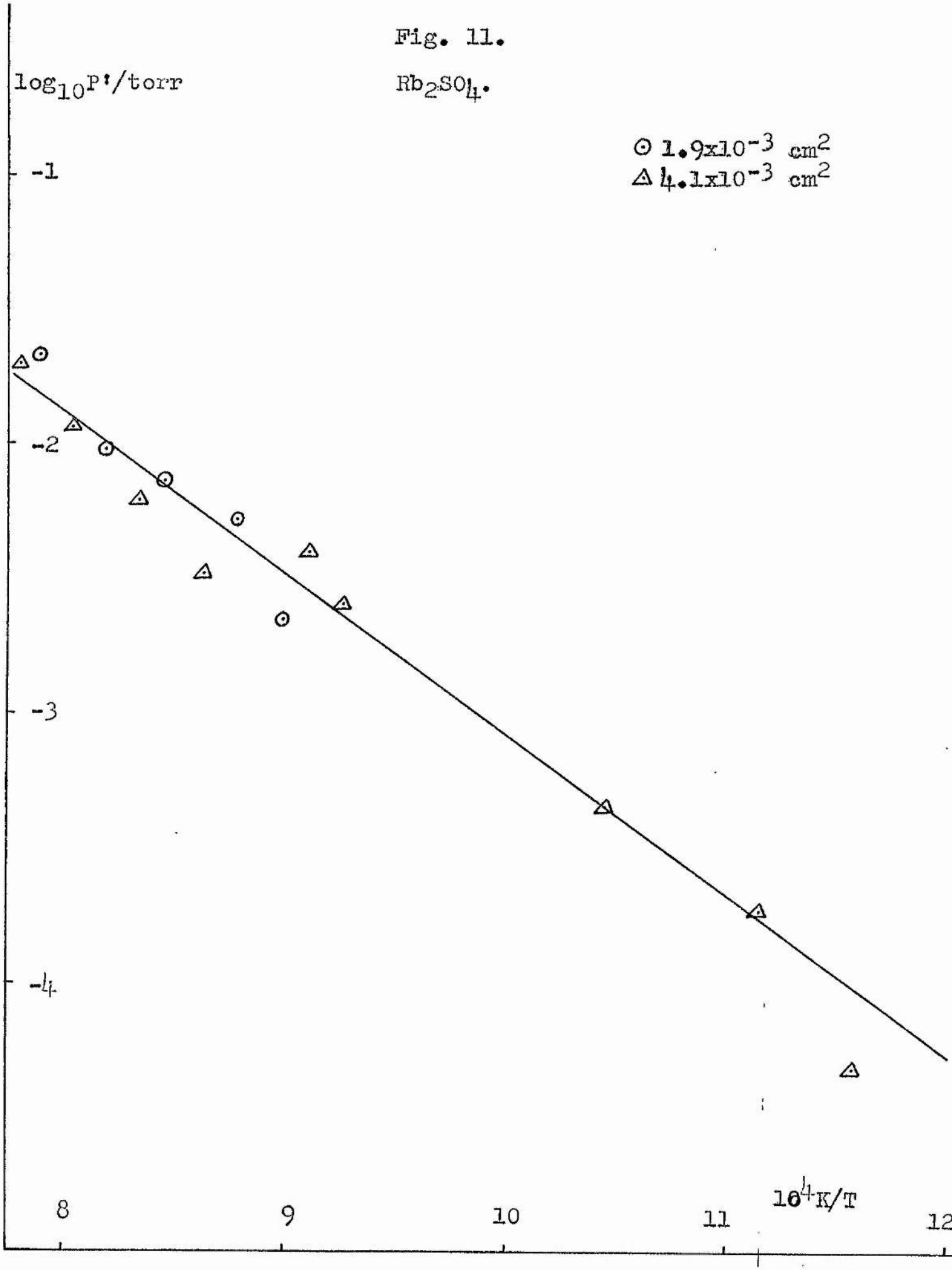

$\log_{10}P'$/torr
Rb_2SO_4.
⊙ 1.9x10^{-3} cm^2
△ 4.1x10^{-3} cm^2
-1
-2
-3
-4
8
9
10
11
12
10^4K/T

Table 5

Caesium sulphate Cs_2SO_4 (Molecular weight 361.87)

T/K	Rate of wt. loss /mg min^{-1}	P'/torr	orifice area/cm^2
993	2.00×10^{-2}	2.39×10^{-3}	4.1×10^{-3}
1025	3.80×10^{-2}	4.61×10^{-3}	
1059	5.00×10^{-2}	6.17×10^{-3}	
1097	5.60×10^{-2}	7.03×10^{-3}	
1186	0.104	1.36×10^{-2}	
1216	0.170	2.25×10^{-2}	
1238	0.218	2.91×10^{-2}	
933	8.98×10^{-3}	2.28×10^{-3}	1.9×10^{-3}
969	1.46×10^{-2}	3.79×10^{-3}	
1040	2.80×10^{-2}	7.50×10^{-3}	
1076	3.00×10^{-2}	8.18×10^{-3}	
1106	3.80×10^{-2}	1.05×10^{-2}	
1148	6.10×10^{-2}	1.72×10^{-2}	

Fig. 12.

Cs_2SO_4.

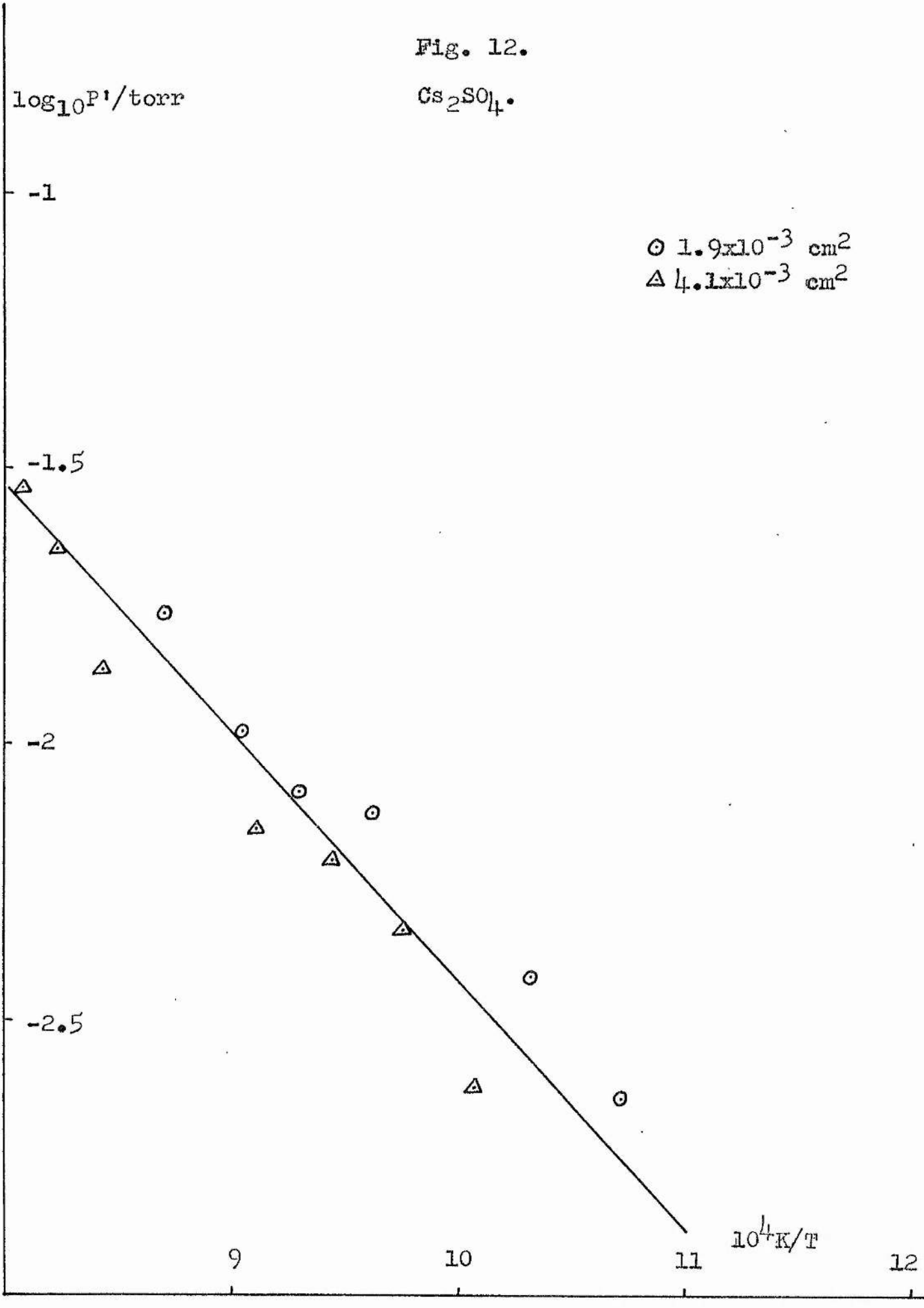


Fig. 13.

Na_2SO_4.

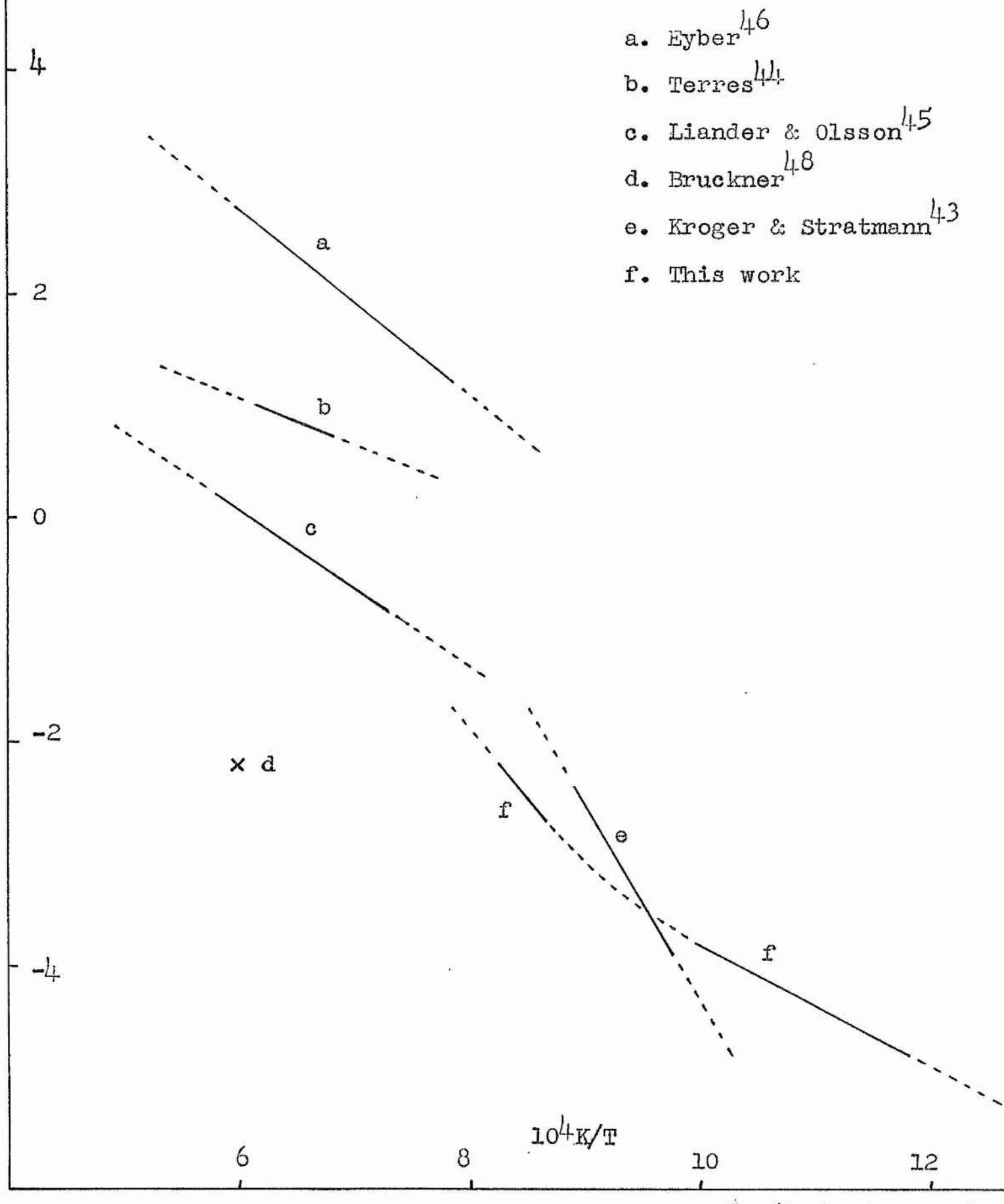
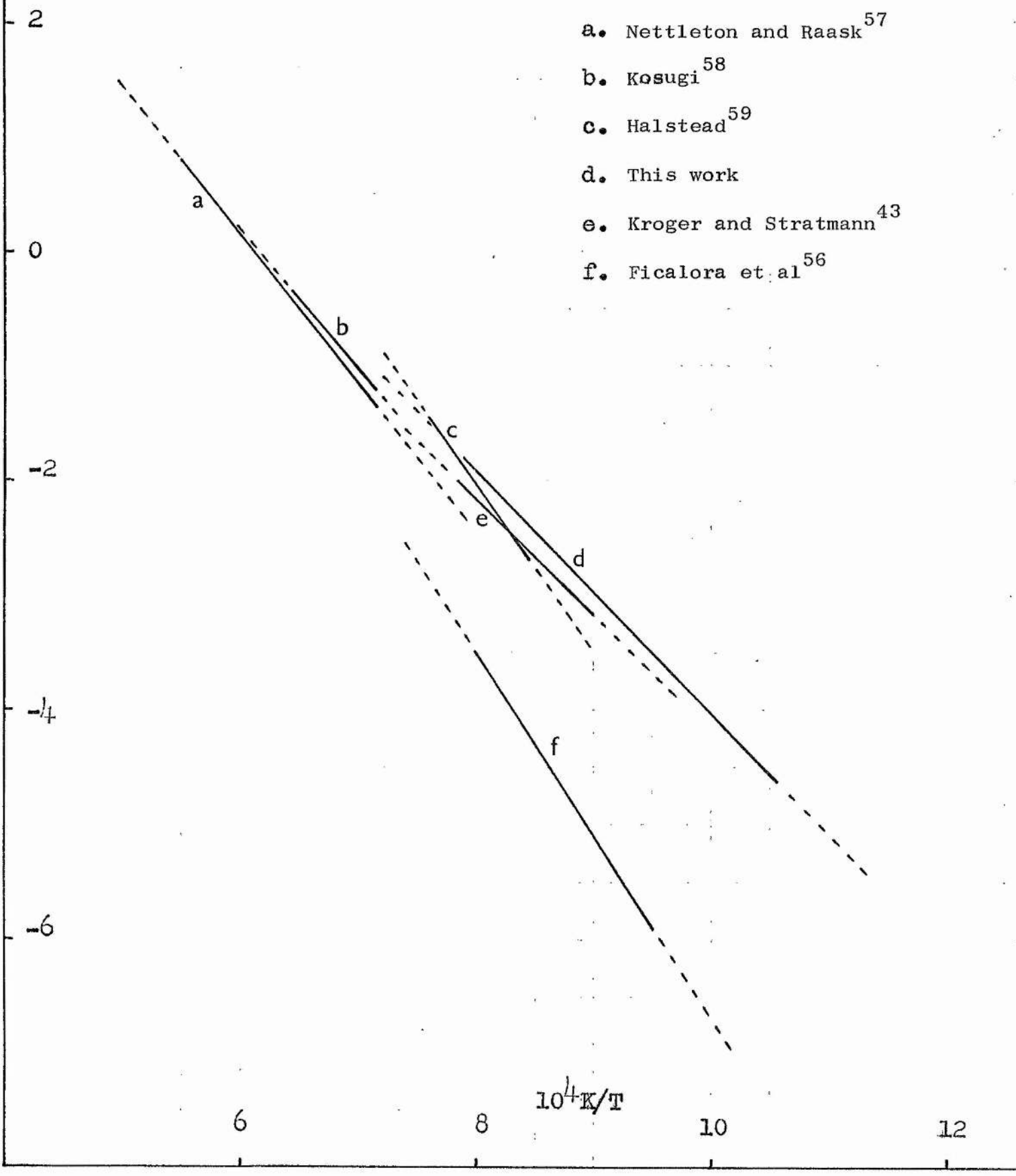


Fig. 14.

K_2SO_4.


log10P'/torr
2
0
-2
-4
-6
a
b
c
d
e
f
a. Nettleton and Raask[57]
b. Kosugi[58]
c. Halstead[59]
d. This work
e. Kroger and Stratmann[43]
f. Ficalora et al[56]
10^4K/T
6
8
10
12

the vapour is mainly 2Na (or 2K) + SO_2 + O_2, the maximum correction to be applied to the effusion data will be an upward shift of $\log_{10} P'$ by 0.3 (= $\log_{10}\sqrt{4}$). Apart from one significantly lower set of mass spectrometric results the whole picture for K_2SO_4 is then reasonably consistent. In view of the satisfactory agreement between the results found here for K_2SO_4 and those previously reported it is considered that the weight loss technique must give a good indication of the magnitude of the true pressure in the case of Na_2SO_4. Fig. 13 indicates that the position for Na_2SO_4 is less satisfactory, but the whole question of the comparison with earlier results will however be discussed more fully later.

The ΔH values, per mole of gas, obtained from the slopes of the $\log_{10} P'$ vs 1/T plots are given in Table 6.

Discussion

The mass spectrometric evidence mentioned earlier seems to rule out any interpretation of the results of the vaporisation of Li_2SO_4 and Na_2SO_4 in terms of

$$M_2SO_4(g) = 2M(g) + SO_2(g) + O_2(g), \qquad (1)$$

because of the absence of any indication of the species M_2SO_4 in the vapour. This is in direct conflict with authors who have assumed

Table 6

ΔH values per mole of gas for the vaporisation of the alkali metal sulphates.

Salt	ΔH/kJ mol^{-1}	ΔH/kcal mol^{-1}
Li_2SO_4 (a) high temp.	221	53
(b) low temp.	36	9
Na_2SO_4 (a) high temp.	226	54
(b) low temp.	111	27
K_2SO_4	211	51
Rb_2SO_4	120	29
Cs_2SO_4	79	19

M_2SO_4 to be the sole vapour species above Na_2SO_4, for example.[43,50]

Consideration was therefore switched to the possible reaction

$$M_2SO_4(s) = 2M(g) + SO_2(g) + O_2(g). \qquad (2)$$

With values of the free energy functions quoted in the JANAF Thermochemical Tables[80], calculations performed for this reaction showed that the expected total pressures are about 3×10^{-4} atmospheres at 1500 K and 7×10^{-7} atmospheres at 1200 K for sodium sulphate; these are of the order of magnitude observed in the 1000°C region. The decomposition of $Na_2SO_4(l)$ at 1200 K to form 2Na(g), $SO_2(g)$, and $O_2(g)$, according to the tables, should be accompanied by a ΔH value of 1220 kJ (292 k cal). The higher slope of the curve in Fig. 9, corresponds to 226 kJ mol^{-1} equivalent to a ΔH value of 904 kJ mol^{-1}. This difference would be expected if the reaction was incomplete at the lower end of the slope used to calculate ΔH. The low temperature slopes obtained for Li_2SO_4 and Na_2SO_4 present a much more formidable problem.

The mass spectrometric evidence for ruling out the presence of Li_2SO_4 and Na_2SO_4 monomers in the vapour phase may be supported using thermochemical data in the following way. Assuming a cuprite type crystal lattice for both sulphates then a Madelung constant of about 4.12 may be applied to both these compounds in the solid state. An approximate value for the corresponding constant for the vapour

phase monomers may be estimated using the simplified model of two positive ions each a distance r from the sulphate ion. This system gives rise to two attractive forces of $2e^2/r$ units each, and one repulsive force of $e^2/2r$ (assuming an intercationic distance of 2r). The net force produced is then $7e^2/2r$ units. The heat of aggregation of $2Na^+$(or Li^+)(g) and SO_4^{2-}(g) to Na_2SO_4(s) (or Li_2SO_4(s)) is in the ratio of 4.12 to 3.5 to the heat of aggregation to Na_2SO_4(g) (or Li_2SO_4(g)) monomers. A rough value for the heat of sublimation from crystal lattice to gaseous monomers may therefore be obtained from 0.62u/4.12 where u is the relevant lattice energy. The lattice energy for Li_2SO_4 is 2123 kJ mol^{-1} (508 k cal mol^{-1}) and for Na_2SO_4 is 1948 kJ mol^{-1} (466 k cal mol^{-1})[81] which give heats of sublimation of 319 kJ mol^{-1} (76.5 k cal mol^{-1}) and 293 kJ mol^{-1} (70 k cal mol^{-1}) respectively. If the monomer species Li_2SO_4(g) and Na_2SO_4(g) were major components of the vapour phase the slopes of the graphs in the low temperature region would be expected to be very much greater. Postulating a polymer of the type $(M_2SO_4)_n$ as a vapour phase constituent does not solve the problem; the small vaporisation enthalpy is reduced yet further to $\Delta H/n$ per M_2SO_4 mole evaporated, since ΔH then has to refer to one mole of the polymer in the vapour phase.

It may be stated here however that applying the argument outlined above to K_2SO_4 gives a heat of sublimation to monomers of 272 kJ mol^{-1} (65 k cal mol^{-1}) which is not far removed from the measured slope of the graph. (See Table 6)

The possibility of the vapour phase reaction

$$2NaO(g) \rightleftharpoons 2Na(g) + O_2(g) \qquad (3)$$

making a contribution was examined using the available values for the free energy functions. At 1000 K the equilibrium constant K_p was found to be 4.5×10^{-3} atmospheres. Assuming a degree of dissociation α then K_p may be expressed by

$$K_p = \alpha^3 P/[2(1-\alpha)^2(1+\alpha/2)],$$

and if the total pressure P is taken as 10^{-6} atmospheres it can be seen that the NaO is completely dissociated at 1000 K. The situation is clearer still at 1200 K and it may be concluded that NaO is not present in the vapour phase.

Calculations performed on the equilibrium

$$Na_2SO_4(s) \rightleftharpoons Na_2S(s \text{ or } l) + 2O_2(g) \qquad (4)$$

reveal that at 1000 K the equilibrium constant for the reaction is of the order of 10^{-35} $(\text{atmospheres})^2$. This means that for pressures of the order of 10^{-6} atmospheres formation of Na_2S is completely

negligible.

The dimerisation of sodium atoms,

$$2Na(g) \rightleftharpoons Na_2(g) \qquad (5)$$

was considered with the help of the thermochemical tables. Assuming α to be the degree of dissociation of the dimer then the following expression for the equilibrium constant K_p holds.

$$K_p = (1-\alpha)(1+\alpha)/4\alpha^2 P$$

or more conveniently

$$1/K_p = 4\alpha^2 P/(1-\alpha^2)$$

At 1000 K, K_p was found to be about 1 (atmosphere)$^{-1}$, or $1/K_p$ about 1 atmosphere. If the total pressure P is once more taken to be of the order of 10^{-6} atmospheres then α is about one and dimerisation of the sodium atoms can be ruled out.

When the formation of lithium dimers was considered in a similar fashion K_p for the reaction

$$2Li(g) \rightleftharpoons Li_2(g) \qquad (6)$$

was found to be about 40 (atmospheres)$^{-1}$ at 1000 K giving a value approaching unity for α and dismissing the possibility of lithium dimerisation.

Calculations involving the various polymers of sulphur show these also to be unlikely vapour phase species.

The lithium sulphate case is particularly acute since the value of ΔH measured from the low temperature slope is very small and reactions of the following type, (listed with ΔH values where available) can not be held to account for the observed behaviour.

$$Li_2SO_4(s) = Li_2O_2(g) + SO_2(g) \qquad 890 \text{ kJ mol}^{-1} \text{ (213 k cal mol}^{-1}\text{)} \quad (7)$$

$$Li_2SO_4(s) = 2Li(g) + O_2(g) + SO_2(g) \qquad 1455 \text{ kJ mol}^{-1} \text{ (348 k cal mol}^{-1}\text{)} \quad (8)$$

$$Li_2SO_4(s) = 2LiO(g) + SO_2(g) \qquad 1304 \text{ kJ mol}^{-1} \text{ (312 k cal mol}^{-1}\text{)} \quad (9)$$

$$Li_2SO_4(s) = Li_2SO_4(g) \qquad 319 \text{ kJ mol}^{-1} \text{ (76.5 k cal mol}^{-1}\text{)} \quad (10)$$

$$Li_2SO_4(s) = Li_2SO_3(g) + \tfrac{1}{2}O_2(g) \quad (11)$$

$$Li_2SO_4(s) = Li_2S(g) + 2O_2(g) \quad (12)$$

$$Li_2SO_4(s) = LiS(g) + Li(g) + 2O_2(g) \quad (13)$$

Kosugi[82] has recently detected Na_2O, but not Na_2SO_4, in the vapour phase mass spectrometrically, and it seems not unreasonable to suggest that the low temperature reactions are

$$Li_2SO_4(s) \rightleftharpoons Li_2O(g) + SO_2(g) + \tfrac{1}{2}O_2(g) \quad (14)$$

$$Na_2SO_4(s) \rightleftharpoons Na_2O(g) + SO_2(g) + \tfrac{1}{2}O_2(g) \quad (15)$$

This preference for the oxide over the sulphate in the vapour on the part of the alkali metals with the smallest cations is in accordance with expectations on simple electrostatic grounds, and gives a qualitative

explanation at any rate of the trend in vapour composition down the alkali metal sulphate series.

Thermodynamic data for $Na_2O(g)$ are wanting, however an estimate of ΔH for the reaction

$$M_2O(g) \rightleftharpoons 2M(g) + \tfrac{1}{2}O_2(g) \qquad (16)$$

can be made using the difference between 4 x (high temperature slope) and 2.5 x (low temperature slope) from Table 6. The values obtained by this method are 794 kJ mol^{-1} (190 k cal mol^{-1}) for Li_2O and 626 kJ mol^{-1} (149 k cal mol^{-1}) for Na_2O, both rather larger than might be expected from the heats of formation of the solid oxides (-596 kJ mol^{-1} and -417 kJ mol^{-1} respectively), JANAF data for $Li_2O(g)$ give a value of 117 k cal mol^{-1} (490 kJ mol^{-1}) for ΔH of (16). Estimates were made of α, the degree of dissociation of $Li_2O(g)$ or $Na_2O(g)$ in the vapour, in the following way.

The numbers of molecules of the various components of the vapour derived from n molecules of $Na_2SO_4(s)$ may be given thus:

$$\begin{array}{ccccccc} Na_2SO_4(s) & \rightleftharpoons & Na_2O(g) & + & SO_2(g) & + & \tfrac{1}{2}O_2(g) \\ -n & & (1-\alpha)n & & n & & n/2 \\ & & \Downarrow & & & & \\ & & 2Na(g) & + & \tfrac{1}{2}O_2(g) & & \\ & & 2\alpha n & & \alpha n/2 & & \end{array} \qquad (17)$$

The partial pressure of each species can then be expressed:-

$Na_2O(g)$	$2(1-\alpha)P/(5+3\alpha)$
$Na(g)$	$4\alpha P/(5+3\alpha)$
$O_2(g)$	$(1+\alpha)P/(5+3\alpha)$
$SO_2(g)$	$2P/(5+3\alpha)$

$$\text{and} \quad K_p = \frac{P_{Na}^2 \times P_{O_2}^{\frac{1}{2}}}{P_{Na_2O}} = \frac{8\alpha^2(1+\alpha)^{\frac{1}{2}}P^{3/2}}{(1-\alpha)(5+3\alpha)^{3/2}}$$

Also for reaction (17) $K = P_{Na_2O} \times P_{SO_2} \times P_{O_2}^{\frac{1}{2}} = \frac{4(1-\alpha)(1+\alpha)^{\frac{1}{2}}P^{5/2}}{(5+3\alpha)^{5/2}}$

For the low temperature line, where reaction (17) only occurs and $\alpha = 0$, P' should be corrected by the $(5/2)^{\frac{1}{2}}$ factor and then $K = 4P^{5/2}/5^{5/2}$ $= P'^{5/2}/(2.5)^{3/4}\sqrt{5}$.

Where the low temperature line is extrapolated

$$K = \frac{4(1-\alpha)(1+\alpha)^{\frac{1}{2}}P^{5/2}}{(5+3\alpha)^{5/2}} = P'^{5/2}_{(\text{extrapolated})}/(2.5)^{3/4}\sqrt{5}$$

where the $P'_{(\text{extrapolated})}$ are no longer experimental values but simply points on the extended low-temperature line. Consequently P is now given not by $P'_{(\text{extrapolated})}(5/2)^{\frac{1}{2}}$ but by $P'_{(\text{experimental})}[(5+3\alpha)/2]^{\frac{1}{2}}$.

$$\text{Hence } K_1 = P'^{5/2}_{\text{extrap.}}/(2,5)^{3/4}\sqrt{5} = \frac{4(1-\alpha)(1+\alpha)^{\frac{1}{2}}}{(5+3\alpha)^{5/2}} \cdot \frac{P'^{5/2}_{\text{exptal}}(5+3\alpha)^{5/4}}{2^{5/4}}$$

$$= \frac{2^{3/4}(1-\alpha)(1+\alpha)^{\frac{1}{2}} P'^{5/2}_{\text{exptal}}}{(5+3\alpha)^{5/4}}$$

$$\text{and finally } \left(\frac{P'_{\text{extrap}}}{P'_{\text{exptal}}}\right)^{5/2} = \frac{(1-\alpha)(1+\alpha)^{\frac{1}{2}}}{(1+3\alpha/5)^{5/4}}$$

The estimates of α found thus enabled values to be calculated for K_p for the equation

$$M_2O(g) \rightleftharpoons 2M(g) + \tfrac{1}{2}O_2(g)$$

which could be represented by

$$\log_{10}K_p = -4.70 \times 10^4 K/T + 34.6 \qquad (18)$$

for $Li_2O(g)$ and

$$\log_{10}K_p = -4.03 \times 10^4 K/T + 26.7 \qquad (19)$$

for $Na_2O(g)$.

Experimentally measured points were used as bases for all these calculations and the values of temperature, α and K_p from which equations (18) and (19) were derived are tabulated below.

For sodium sulphate

T/K	α	$K_p/atm^{3/2}$
1200	0.92	2.45×10^{-7}
1164	0.845	4.21×10^{-8}
1151	0.30	3.65×10^{-10}
1135	0.38	5.80×10^{-10}
1124	0.72	6.45×10^{-9}

For lithium sulphate

T/K	α	$K_p/atm^{3/2}$
1214	0.997	5.30×10^{-5}
1176	0.994	1.28×10^{-5}
1163	0.97	8.60×10^{-7}
1130	0.91	1.14×10^{-7}
1127	0.88	6.50×10^{-8}

The dependence of the measured vapour pressure upon the temperature is embodied in the following equations for Na_2SO_4 and Li_2SO_4.

Na_2SO_4 high temperature region

$$\log_{10}P'/torr = -(1.173\pm0.30) \times 10^4 \ K/T + (7.43\pm0.11)$$

low temperature region

$$\log_{10}P'/torr = -(0.575\pm0.06) \times 10^4 K/T + (2.00\pm0.05)$$

Li_2SO_4 high temperature region,

$$\log_{10}P'/torr = -(1.146\pm0.2) \times 10^4 \ K/T + (7.67\pm0.12)$$

low temperature region

$$\log_{10}P'/torr = -(0.185\pm0.03) \times 10^4 \ K/T -(1.31\pm0.06)$$

This phenomenon of a change in slope of these curves has not previously been reported. Reference to Fig. 13 will show that the results reported here for Na_2SO_4 are fairly close to those of Kroger and Stratmann[43] and of Liander and Olsson[45]. Bruckner's[48] result is an average of

several figures obtained from different flow rates with an atmosphere of $SO_2 + \frac{1}{2}O_2$, and would therefore be lower than might be expected in a vacuum. The highest results of all were found by indirect calculation[46], and Terres[44] does not describe his experimental procedure.

The vapour pressure results of the experiments performed on K_2SO_4 are described by the equation

$$\log_{10} P'/\text{torr} = -(1.097 \pm 0.05) \times 10^4 \; K/T + (6.82 \pm 0.04)$$

Apart from the low set of results obtained mass spectrometrically[56], and mentioned earlier, the results of this work are in good agreement with those found earlier by a variety of methods.

The Rb_2SO_4 vapour pressures are related to the temperature by

$$\log_{10} P'/\text{torr} = -(0.623 \pm 0.06) \times 10^4 \; K/T + (3.11 \pm 0.08)$$

and for Cs_2SO_4 the relation is

$$\log_{10} P'/\text{torr} = -(0.412 \pm 0.06) \times 10^4 \; K/T + (1.73 \pm 0.05)$$

The only previously reported work on these compounds which is even vaguely comparable is that of Ficalora et al[56]. These investigators report values for the heat of sublimation of rubidium and caesium sulphates of 69.7 k cal mol^{-1} and 63.9 k cal mol^{-1} respectively. These values differ markedly from the values found here (see Table 6). Also the absolute values of the measured vapour pressure as reported by Ficalora et al, are two orders of magnitude lower than those found during the course of this work. These striking differences are,

at the moment, unaccountable.

For all the alkali metal sulphates at least two, and sometimes three, different orifice sizes were used but for each substance a unique line was observed. This indicates a large value for the evaporation coefficient.

All the above equations relating to experimental results describe the best straight line through the points calculated by the least mean squares method on an I.B.M. 360/44 computer. The limits represent the 95% confidence limits.

Results and discussion of torsion experiments

Sodium sulphate, potassium sulphate, and rubidium sulphate failed to give a measurable response during the course of this experiment. (The difficulties attendant upon these measurements have been mentioned earlier). However results were obtained for lithium sulphate and caesium sulphate and are shown in Tables 7 and 8, and Figs. 15 and 16. The value of this experiment lies in the fact that a value need not be assumed for the molecular weight of the vapour species. In fact, by using this method in combination with the Knudsen weight loss method a value may be calculated for the vapour molecular weight. Owing to the imperfections of the experimental system the range of values for the molecular weight is rather large. The results

Table 7

Lithium sulphate Li_2SO_4

T/K	P/torr
886	6.75×10^{-4}
931	1.58×10^{-3}
976	1.85×10^{-3}

Fig. 15.

$\log_{10}P$ /torr

Li_2SO_4 (torsion).

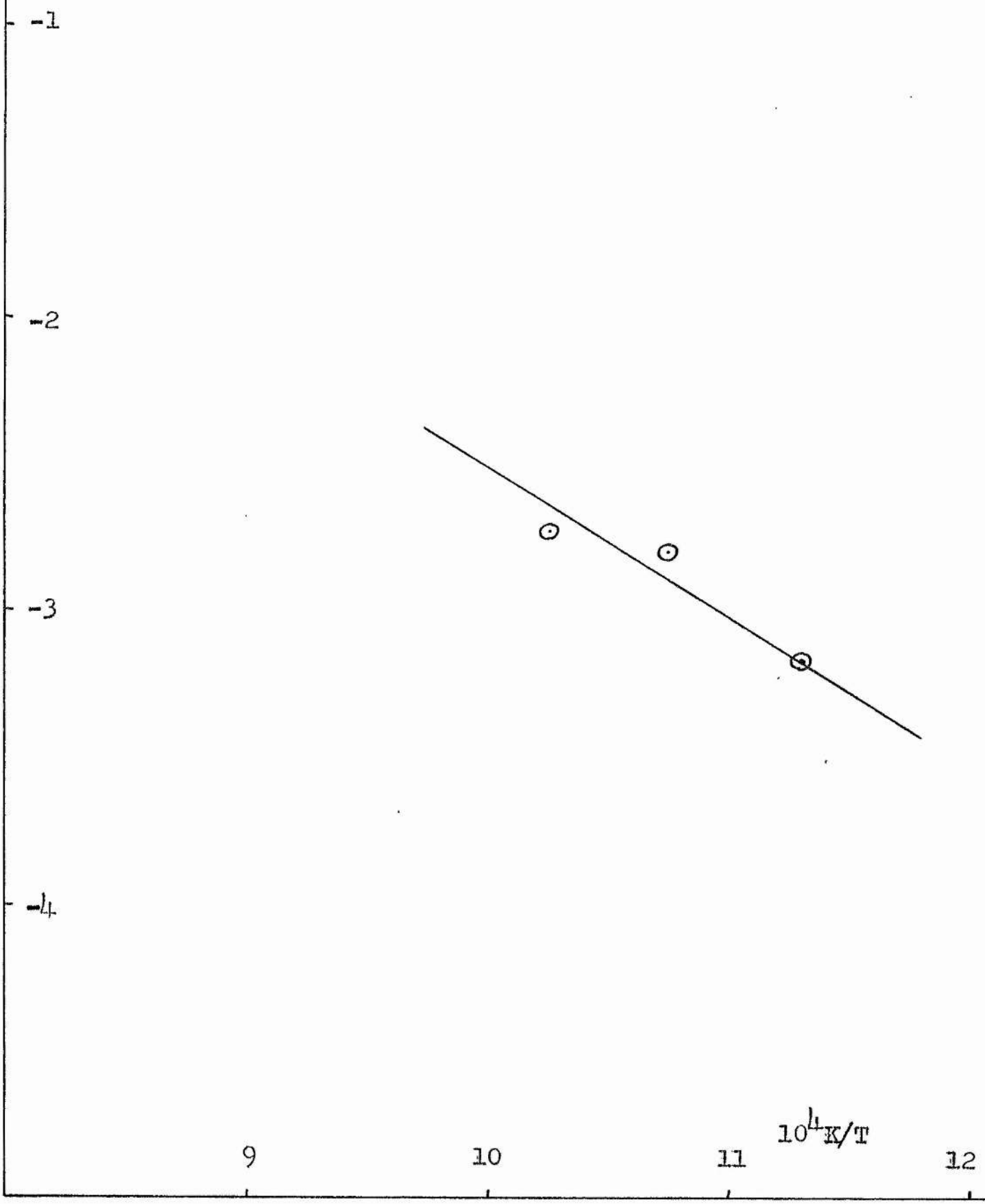
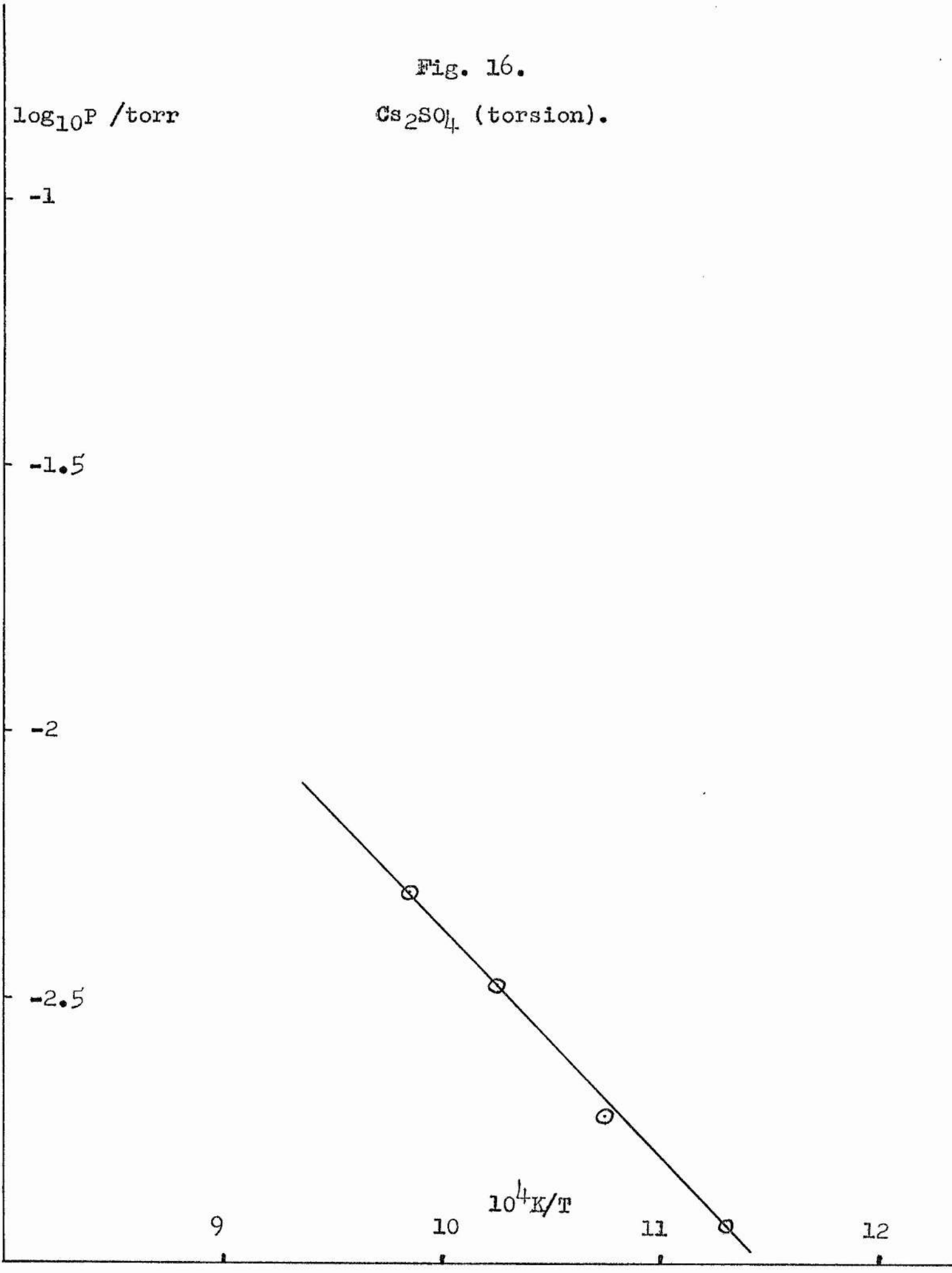


Table 8

Caesium sulphate Cs_2SO_4

T/K	P/torr
886	1.19×10^{-3}
931	1.90×10^{-3}
976	3.35×10^{-3}
1016	5.05×10^{-3}

Fig. 16.



for Li_2SO_4 are tabulated below.

T/K	M
886	38.5
931	11.0
976	11.8

These values give a mean vapour molecular weight of 21. (Complete formation of $2Li(g) + SO_2(g) + O_2(g)$ would require a mean molecular weight of 27.5)

The most that can be said for this value is that it lends tentative support to the thesis that lithium sulphate does not vaporise as Li_2SO_4 entities. The equation describing the dependence of the torsion vapour pressure on temperature is

$$\log_{10}P/\text{torr} = -0.428 \times 10^4\ K/T + 1.71$$

yielding a ΔH value of 82 kJ (19.6 kcal)(per mole of gas) by the torsion method.

For caesium sulphate the corresponding results are,

T/K	M
886	243
931	303
976	267
1016	269

giving a mean molecular weight for the vapour species of 270.

This value encourages the belief that caesium sulphate evaporates predominantly as the Cs_2SO_4 species. The relation between the torsion vapour pressure and temperature is

$$\log_{10} P/\text{torr} = -0.440 \times 10^4 \, K/T + 2.03$$

giving a ΔH value of 84 kJ (20.1 k cal)(per mole of gas), by the torsion method.

These ΔH values compare with 36 kJ mol^{-1} and 79 kJ mol^{-1} for Li_2SO_4 and Cs_2SO_4 respectively found from the graphs of the results of the weight loss method. If the ΔH value found by the torsion method for Li_2SO_4 is now used in conjunction with the value found for the high temperature region by the weight loss method then ΔH for the reaction.

$$Li_2O(g) \rightleftharpoons 2Li(g) + \tfrac{1}{2}O_2(g)$$

becomes 683 kJ mol^{-1} (163 k cal mol^{-1}). However as this is based on a graph of only three points it should be treated with circumspection.

Summary

The avowed intention of this study was to attempt to assess the relative merits of existing data on the vaporisation properties of the alkali metal sulphates. In the event it may fairly be said that

unequivocal concord with previously published results exists only in the case of K_2SO_4. In the case of Li_2SO_4 and Na_2SO_4 direct comparison is difficult owing to the lack of thermochemical data for $Li_2SO_4(s)$ and $Na_2O(g)$ in particular. Agreement was not found between calculations using tabulated data for $Li_2O(g)$ and calculations from measurements made here. As was mentioned earlier the ΔH's for the reactions of the type

$$M_2O(g) \rightleftharpoons 2M(g) + \tfrac{1}{2}O_2(g)$$

found here were rather larger than might be anticipated from the heats of formation of the solid oxide, but on the other hand total confidence in the available data for alkali metal oxides may be misplaced for the following reasons. The chemical nature of the compounds and the ease of peroxide formation makes them difficult substances to work with but more particularly it has been observed that vapour pressure data from mass spectrometric work have sometimes differed from the results of effusion and transpiration experiments by several orders of magnitude. Thermochemical data found from the results of mass spectrometric work may not therefore carry complete conviction. The value for the heat of sublimation of Li_2O, for example, is variously reported as 102 and 50 k cal mol^{-1}.

Notwithstanding the possibly high values of ΔH for the relevant

reactions and, in any case, with the assumption that ΔH^{o}_{298} is the same as ΔH at the reaction temperature, values of the free energy function $[-(G^{o}-H^{o}_{298})/T]$ were calculated for $Li_2SO_4(s)$, $Li_2O(g)$, and $Na_2O(g)$. In the case of the oxides values for K_p at various temperatures were obtained from equations (18) and (19) enabling $-\Delta G^{o}/T$ to be evaluated, and for Li_2SO_4 the Kp of equation (18) was combined with that of (17) to give $-\Delta G^{o}/T$ for the reaction

$$Li_2SO_4(s) \rightleftharpoons 2Li(g) + SO_2(g) + O_2(g).$$

The free energy function for Li_2SO_4 may be calculated from the values in the JANAF tables for Li(g), $SO_2(g)$, and $O_2(g)$ by means of the expression

$$[-(G^{o}-H^{o}_{298})/T]_{Li_2SO_4(s)} = 2[-(G^{o}-H^{o}_{298})/T]_{Li(g)} + [-(G^{o}-H^{o}_{298})/T]_{SO_2(g)}$$

$$+ [-(G^{o}-H^{o}_{298})/T]_{O_2(g)} - \Delta H^{o}_{298}/T - (-\Delta G^{o}/T)$$

The values obtained by this method are given below.

	1100 K	1150 K	1200 K	1250 K	
$Li_2SO_4(s)$	72.94	71.79	71.56	71.61	cal mol^{-1} deg^{-1}
$Na_2O(g)$	16.40	13.24	11.83	10.02	cal mol^{-1} deg^{-1}
$Li_2O(g)$	-37.64	-38.48	-38.75	-39.33	cal mol^{-1} deg^{-1}

(The tabulated values for $Na_2SO_4(s)$ are 61.45 cal mol^{-1} deg^{-1} at 1100 K

and 64.29 cal mol^{-1} deg^{-1} at 1200 K.)

Recent mass spectrometric evidence indicates the presence of an oxide in the vapour above Na_2SO_4 and the curvature in the log P vs I/T graphs for Na_2SO_4 and Li_2SO_4 lends weight to belief in a second decomposition at higher temperatures. The figures derived above all show an incorrect tendency to decrease with rising temperature and the negative values obtained for $Li_2O(g)$ underline their sensitivity to a high ΔH value. A consistent interpretation of these observations in terms of the formation and decomposition of Na_2O and Li_2O has been attempted but is clearly discountenanced, in the case of Li_2O at any rate, by the large values of ΔH measured here. Calculations using JANAF data performed on the reaction

$$LiO(g) \rightleftharpoons Li(g) + \tfrac{1}{2}O_2(g)$$

give values for Kp of 4.4×10^{-3} (atmospheres)$^{\frac{1}{2}}$ at 1000 K and 2.0×10^{-2} (atmospheres)$^{\frac{1}{2}}$ at 1200 K, indicating that the species LiO may contribute to the vapour phase. Simiarly the reaction

$$Li_2O_2(g) \rightleftharpoons 2LiO(g) \qquad \Delta H \text{ 410 kJ } mol^{-1} \text{ (98.2 kcal } mol^{-1})$$

has Kp values of 1.4×10^{-14} atmospheres at 1000 K and 4.5×10^{-11} atmospheres at 1200 K apparently favouring the existence of the dimer

Li_2O_2 at the total pressure of 10^{-6} atmospheres. A simple calculation shows that extra stability is conferred by the increased number of attractions and repulsions involved in the formation of the tetramer Li_4O_4. The estimated ΔH for the reaction

$$Li_4O_4(g) \rightleftharpoons 4LiO(g)$$

is 1225 kJ mol^{-1} (293 k cal mol^{-1}) and for the decomposition

$$Li_2SO_4(s) = \tfrac{1}{2}Li_4O_4(g) + SO_2(g)$$

is 685 kJ mol^{-1} (164 k cal mol^{-1}).

It seems clear that although the evidence suggests decomposition and oxide formation the reactions cannot be uniquely described in terms of any of the oxide types M_2O, MO, or $(MO)_n$. It is difficult to believe, however, that the vaporisation process of such an apparently simple system as Li_2SO_4 is not described by one, or a combination of two or more, of the reactions (7) to (13). Since the available data rule the formation of Na_2S completely out of court, what has just been said about oxide formation makes the most probable course of events still appear to be formation and decomposition of an oxide with accompanying evolution of sulphur dioxide. This means that either the data which form the basis of all the calculations carried out above or the values calculated from the experimental results are wrong. It has been mentioned earlier that quantitatively the results of mass spectrometric work have

been at variance with results found by other means, and that any free energy data derived by this method are attended by an element of doubt. This is the more puzzling since qualitatively the results of mass spectrometric and other work are generally in accord. It must be conceded however that the changes necessary in the tabulated data in order to bring about agreement between a postulated reaction scheme and the results found here for lithium sulphate are so radical that this is unlikely to be the only source of error.

The work on all the alkali metal sulphates was carried out in the same apparatus and the search for an experimental artefact must take into account the observation that for K_2SO_4 lower pressures were measured at temperatures comparable to those to which Li_2SO_4 was subjected. The same was true for $MgSO_4$ and in both cases very satisfactory results were obtained. The error then is not due to any limitation in the measuring of pressure or temperature. It is conceivable that there is attack by the products of decomposition of Li_2SO_4 upon the spinel crucible.

In the case of both Rb_2SO_4 and Cs_2SO_4 mass spectrometric work indicates a preponderance of $Rb_2SO_4(g)$ and $Cs_2SO_4(g)$ species in the vapour phase. On the other hand, the same work attributes values to the vapour pressure two orders of magnitude lower than the results found here. The results of the torsion experiments favour the appearance of $Cs_2SO_4(g)$

as a vapour phase species; but use of the available lattice energy data (1756 kJ mol^{-1} (420 k cal mol^{-1}) for Rb_2SO_4 and 1684 kJ mol^{-1} (403 k cal mol^{-1}) for Cs_2SO_4)[81] in the way detailed for Na_2SO_4 yields values for the heats of vaporisation to monomers of 264 kJ mol^{-1} (63.2 k cal mol^{-1}) for Rb_2SO_4 and 253 kJ mol^{-1} (60.6 k cal mol^{-1}) for Cs_2SO_4. These values are considerably in excess of those found in Table 6. The difficulties with these compounds too are unresolved.

2. Magnesium and Calcium sulphates.

Results of Knudsen effusion experiments

The results of the weight loss experiments on these salts are given in Tables 9 and 10, and they are presented graphically in Figs. 17 to 20. In all these figures $\log_{10}P'$ is plotted against 1/T. In Figs. 17 and 19, P' is the value calculated using a vapour phase molecular weight corresponding to the species MSO_4 for each compound, and in Figs. 18 and 20, P'' is the value calculated using an average vapour phase molecular weight of 53.3 for $MgSO_4$ and for $CaSO_4$ based on the decompositions

$$MgSO_4 = MgO + SO_2 + \tfrac{1}{2}O_2$$

$$CaSO_4 = CaO + SO_2 + \tfrac{1}{2}O_2$$

The results found for $CaSO_4$ may be represented by a single straight line

Table 9

Magnesium sulphate $MgSO_4$ (Molecular weight 120.4)

T/K	Rate of wt. loss /mg min^{-1}	P'/torr	Orifice area/cm^2
934	3.00×10^{-3}	6.04×10^{-4}	4.1×10^{-3}
952	4.67×10^{-3}	9.49×10^{-4}	
996	1.25×10^{-2}	2.60×10^{-3}	
1036	4.00×10^{-2}	8.49×10^{-3}	
1064	8.71×10^{-2}	1.87×10^{-2}	
1086	0.155	3.37×10^{-2}	
954	1.00×10^{-2}	4.46×10^{-3}	1.9×10^{-3}
974	1.20×10^{-2}	5.41×10^{-3}	
1006	4.30×10^{-2}	1.97×10^{-2}	
1019	6.40×10^{-2}	2.95×10^{-2}	
1040	0.112	5.22×10^{-2}	
1066	0.186	8.77×10^{-2}	
945	8.89×10^{-3}	8.62×10^{-3}	8.9×10^{-4}
974	1.40×10^{-2}	1.38×10^{-2}	
1006	3.71×10^{-2}	3.72×10^{-2}	
1025	6.57×10^{-2}	6.64×10^{-2}	
1050	0.100	1.02×10^{-1}	

Fig. 17.

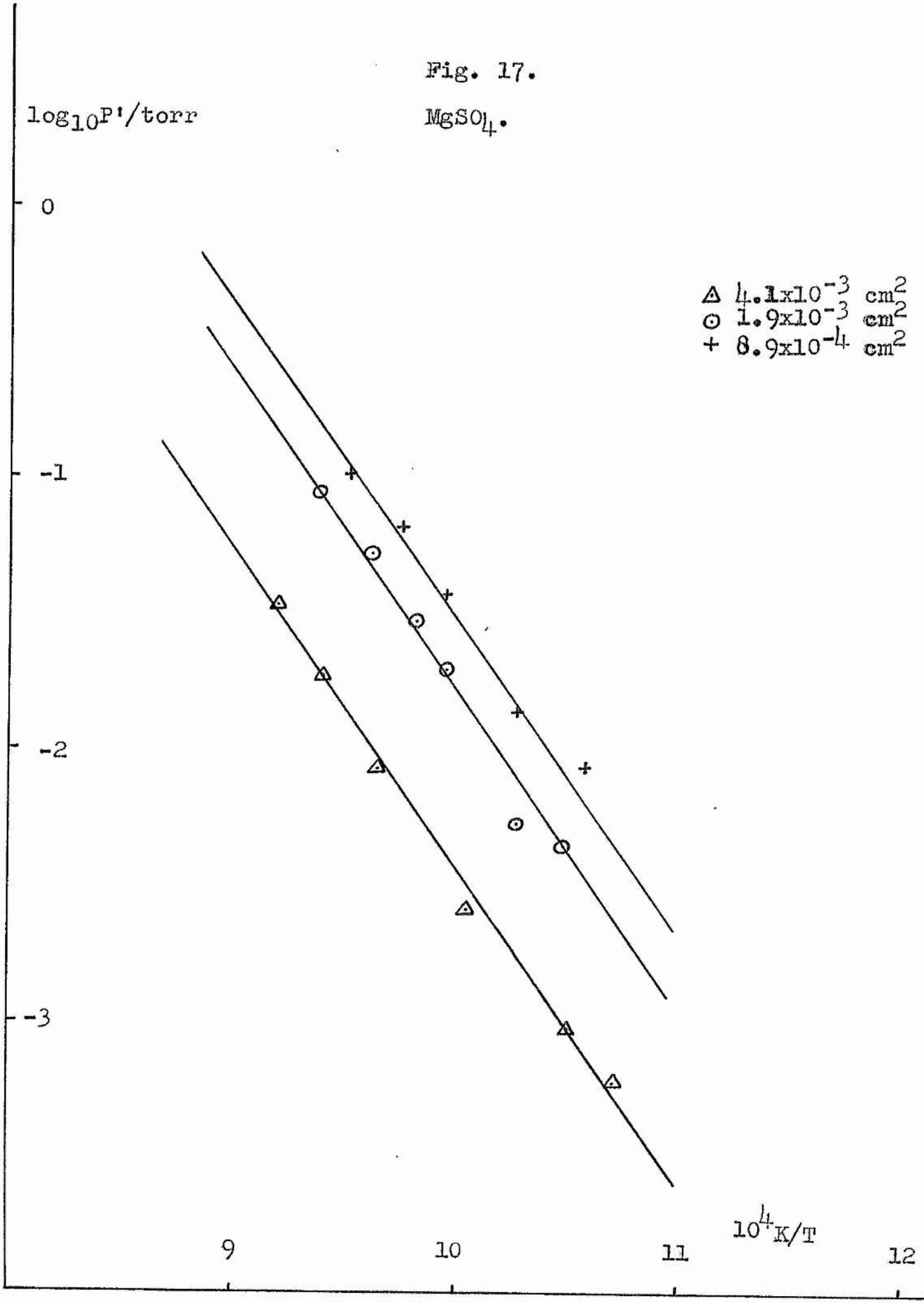

$\log_{10}P'/\text{torr}$
$MgSO_4$.
0
-1
-2
-3
Δ 4.1x10^{-3} cm^2
⊙ 1.9x10^{-3} cm^2
+ 8.9x10^{-4} cm^2
9
10
11
12
10^4K/T

Fig. 18.

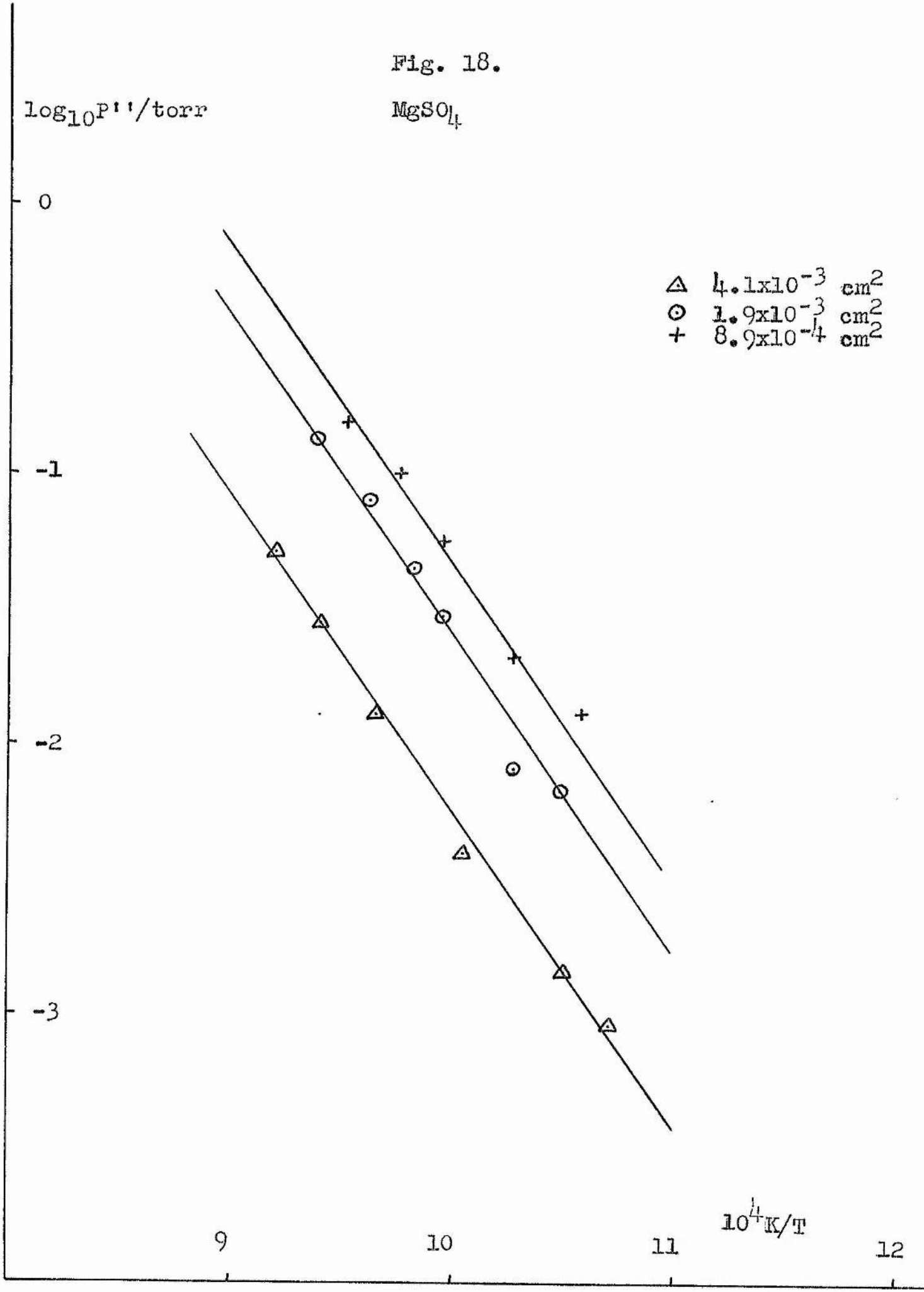

$\log_{10}P''/torr$
$MgSO_4$
0
-1
-2
-3
$4.1x10^{-3}$ cm^2
$1.9x10^{-3}$ cm^2
$8.9x10^{-4}$ cm^2
9
10
11
12
$10^4 K/T$

Table 10

Calcium sulphate $CaSO_4$ (Molecular weight 136.2)

T/K	Rate of wt. loss /mg min^{-1}	P'/torr	Orifice area/cm^2
1054	5.14×10^{-3}	1.03×10^{-3}	4.1×10^{-3}
1089	6.67×10^{-3}	1.36×10^{-3}	
1117	6.67×10^{-3}	1.38×10^{-3}	
1106	4.00×10^{-3}	1.80×10^{-3}	1.9×10^{-3}
1147	8.57×10^{-3}	3.94×10^{-3}	
1246	3.00×10^{-2}	1.44×10^{-2}	
1026	1.00×10^{-3}	4.34×10^{-4}	
1268	2.12×10^{-2}	1.03×10^{-2}	

Fig. 19.

$CaSO_4$.

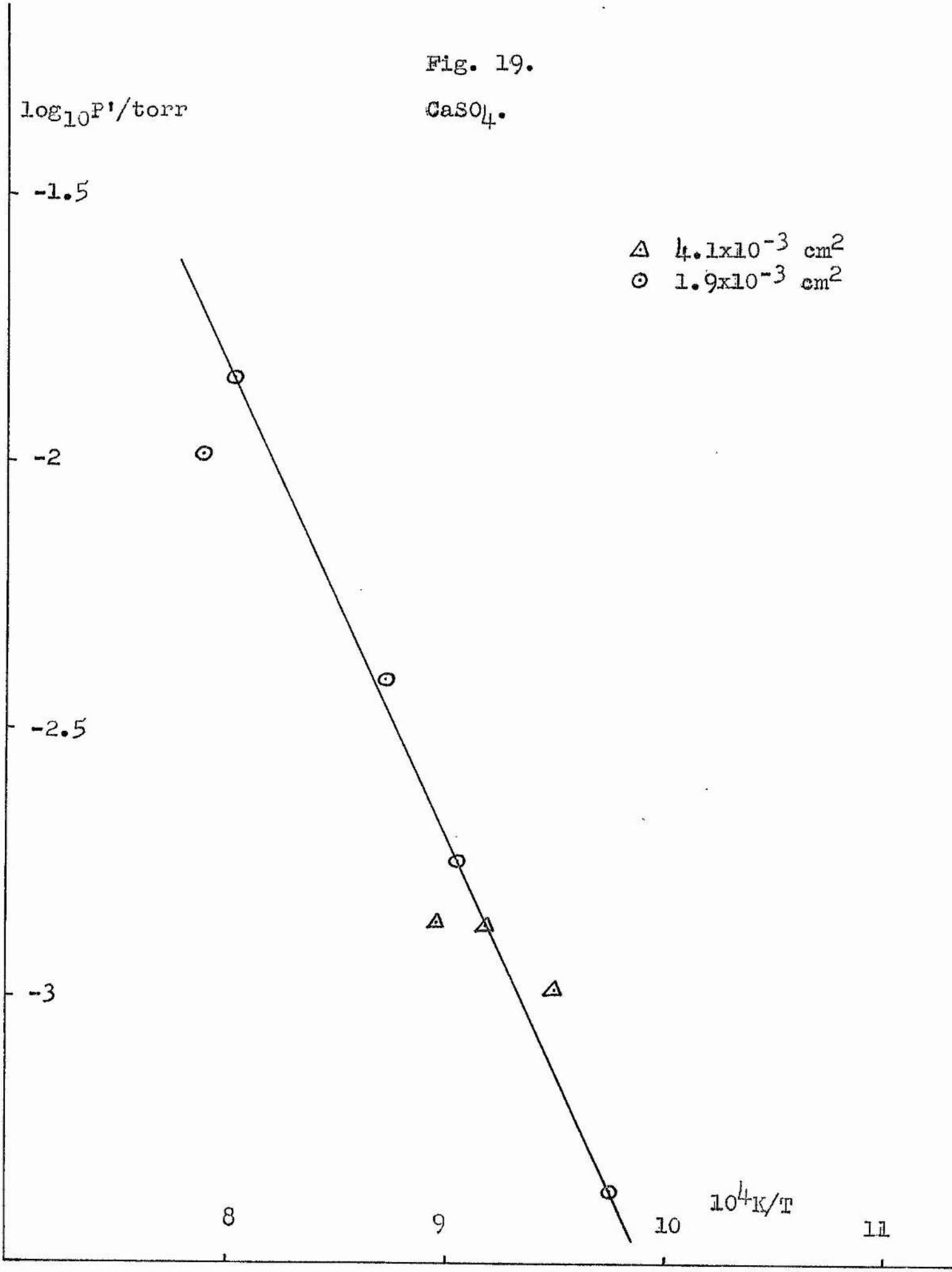
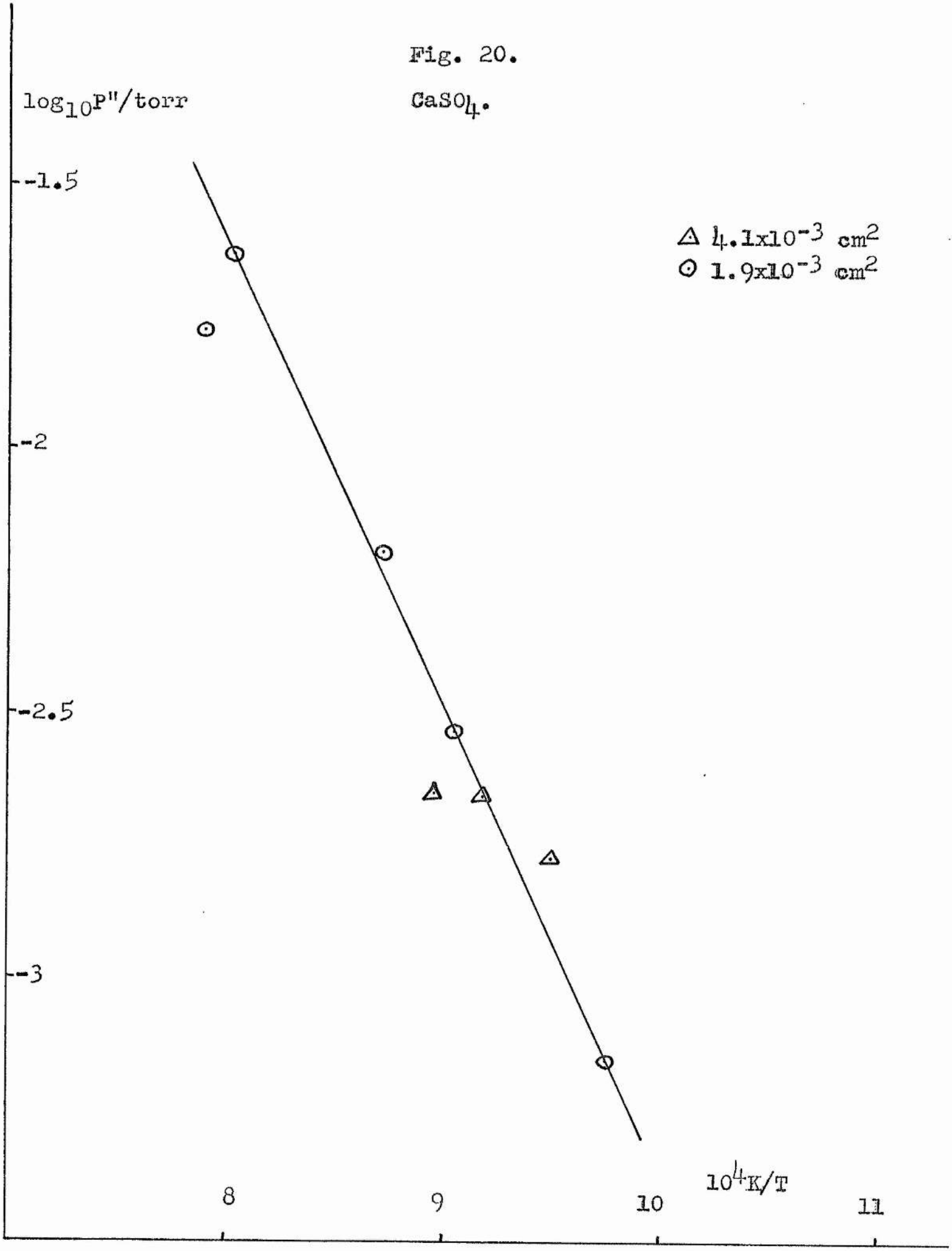


Fig. 20.

$CaSO_4$.



but those for $MgSO_4$ illustrate the first instance found in this series of experiments where different orifice areas produce different lines parallel to each other. This phenomenon is thought to be related to the value of the evaporation coefficient of $MgSO_4$ and will be discussed later. Neither compound melts in the experimental temperature range.

Figs. 21 and 22 illustrate the comparison of the results found here for $MgSO_4$ and $CaSO_4$ with those of former authors[76-79]. As will be seen, the values found here for $MgSO_4$ using the smallest orifice agree well with the literature values but the dependence of the pressure upon the Knudsen orifice area has not previously been reported. An effort to calculate the evaporation coefficient of $MgSO_4$ will be mentioned later, together with the more complex position of $CaSO_4$ vis-à-vis the extant literature. The Analar starting materials were $MgSO_4.7H_2O$ and $CaSO_4.2H_2O$.

Discussion

Starting with the possible reaction

$$MgSO_4(s) = MgO(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \qquad (20)$$

calculations using the JANAF Thermochemical Tables revealed that the total pressure above $MgSO_4$ at 1000 K is expected to be 6×10^{-4} atmospheres and 4.7×10^{-2} atmospheres at 1200 K. These values are of

Fig. 21.

$MgSO_4$.

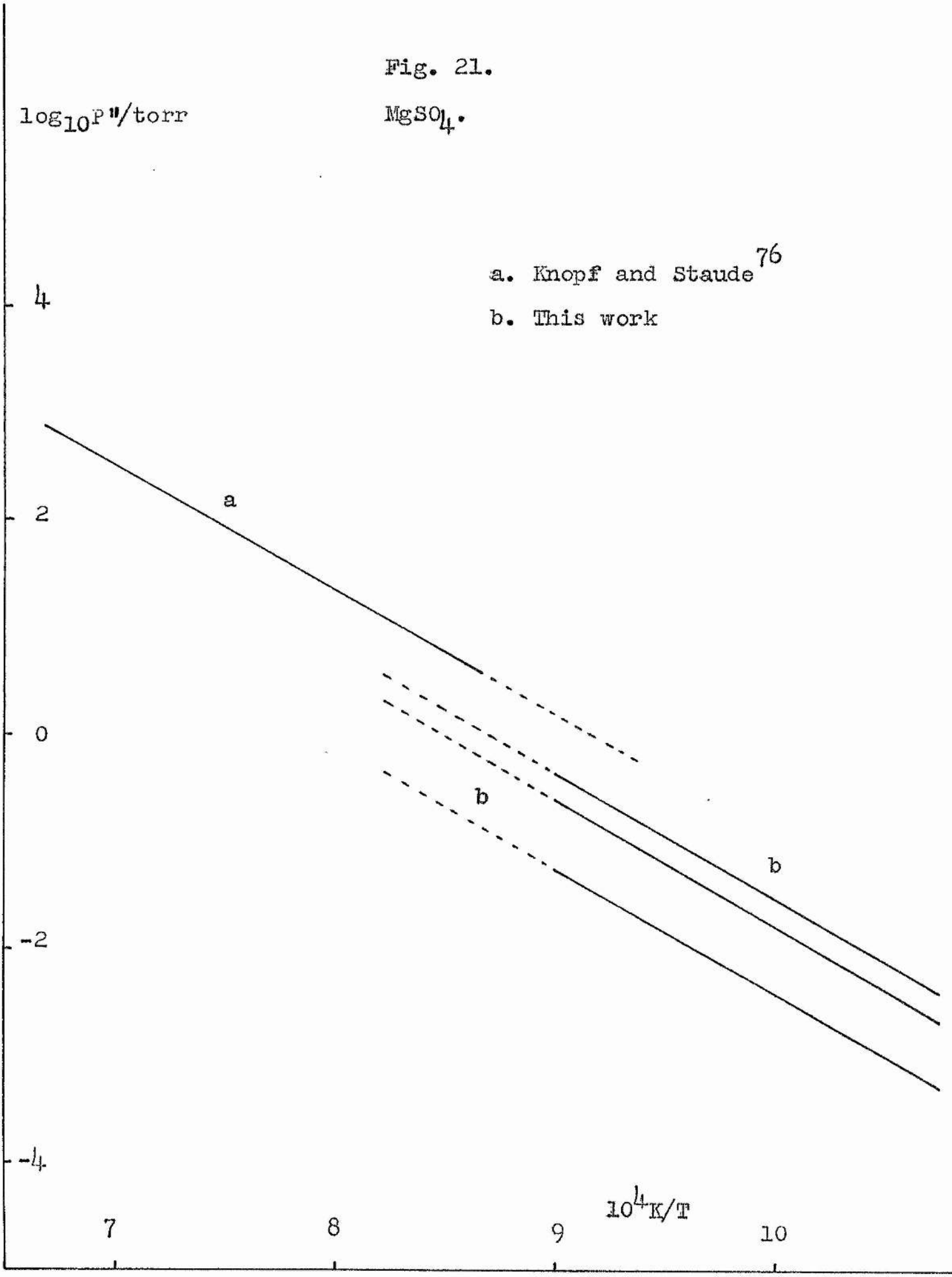
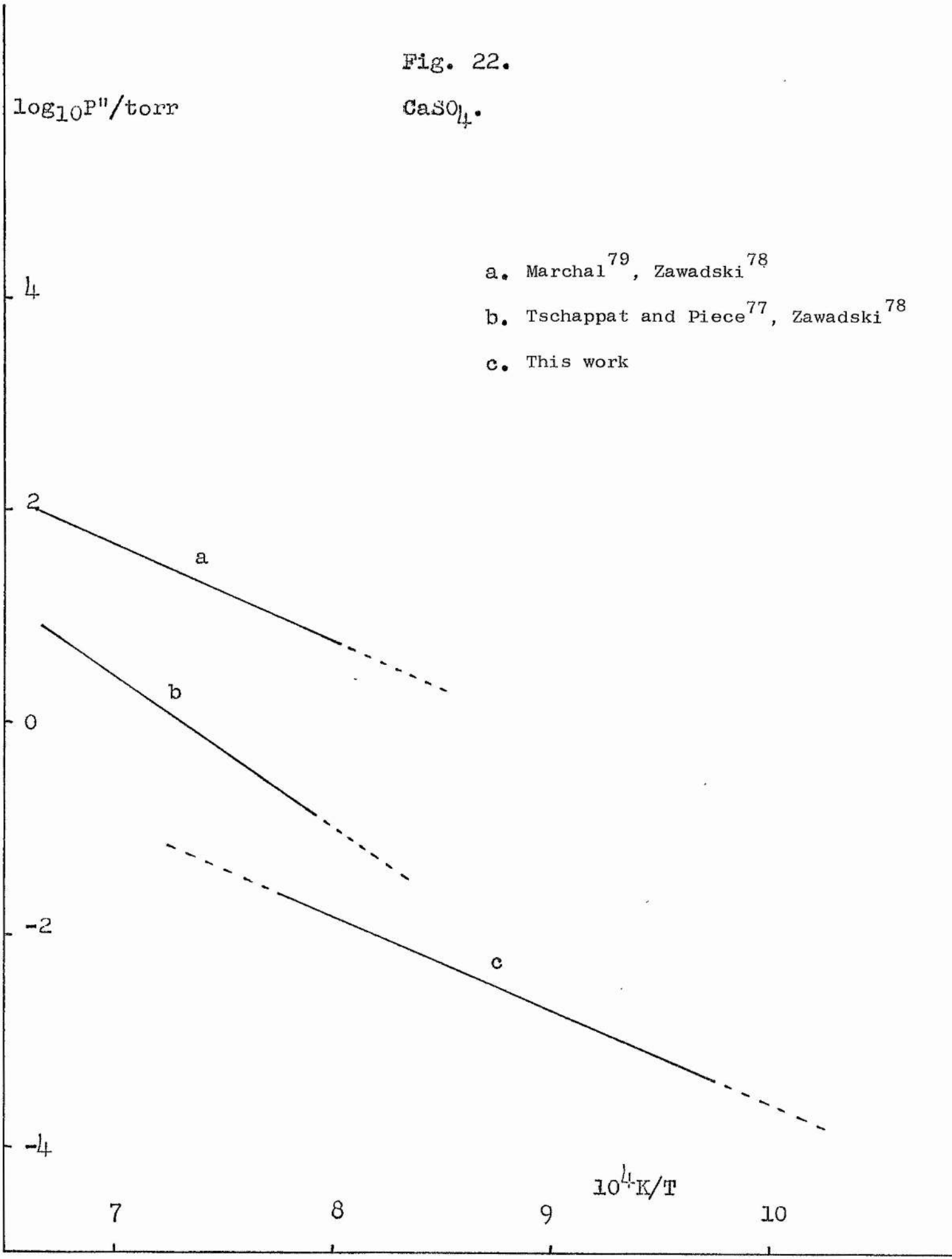

log10P"/torr
a. Knopf and Staude[76]
b. This work
4
2
0
-2
-4
a
b
b
7
8
9
10
10^4 K/T

Fig. 22.

$CaSO_4$.



a. Marchal[79], Zawadski[78]

b. Tschappat and Piece[77], Zawadski[78]

c. This work

the order of magnitude observed here. The ΔH value of the decomposition (20) should, according to these tables, be 363.2 kJ mol^{-1} (86.9 k cal mol^{-1} at 1200 K. The average slope of the graphs in Fig. 17 yields a figure of 225 kJ mol^{-1} equivalent to a ΔH value of 337.3 kJ mol^{-1} (80.7 k cal mol^{-1}). This agreement is close enough to reinforce the view that (20) describes the reaction accurately. The connection between vapour pressure and temperature for the three graphs of $MgSO_4$ may be represented by,

$$\log_{10}P'/\text{torr} = -(1.16 \pm 0.11) \times 10^4 K/T + (9.18 \pm 0.08)$$

$$\log_{10}P'/\text{torr} = -(1.27 \pm 0.21) \times 10^4 K/T + (10.91 \pm 0.10)$$

$$\log_{10}P'/\text{torr} = -(1.07 \pm 0.18) \times 10^4 K/T + (9.24 \pm 0.16).$$

The graph found by using the smallest orifice is in good agreement with the results of Knopf and Staude[76] as portrayed in Fig. 21.

The only anomaly requiring explanation is the dependence of the vapour pressure on the area of the Knudsen effusion orifice. It might help to clarify the situation if each measured pressure were to be regarded as a pseudo-equilibrium vapour pressure approaching the true equilibrium vapour pressure as the area of the orifice approaches zero. Thus the equilibrium vapour pressure, P_{eq}, may be estimated by plotting the observed steady state pressure, P_m, as a function of the orifice area and extrapolating to zero orifice area. The relation, due to Motzfeld[8],

$$P_{eq}/P_m = 1 + f/\alpha$$

where f is the ratio of orifice area to cell cross section area, may now be used to determine a value for α, the vaporisation coefficient. This was done for the three temperatures 1053, 1000, and 952K and yielded the average value of 5.9×10^{-3} for the vaporisation coefficient, α.

The whole concept of accommodation coefficients (vaporisation and condensation) has been discussed at length earlier but it may be reiterated that most metals and simple salts are found to have values close to unity for these coefficients. For example, the lack of dependence of the vapour pressure of the alkali metal sulphates upon the orifice area is indicative of values approaching unity of the evaporation coefficients of these compounds. Another magnesium compound, the hydroxide has been found by Kay and Gregory[26] to have a low vaporisation coefficient, 1.8×10^{-3}. Discussing this low value these authors mention an observation that the large cleavage surfaces of brucite crystals do not participate in the initial stages of the decomposition; decomposition appears to occur largely at the edges. Perhaps in the case of magnesium sulphate it is the kinetics of the formation of suitable sites for magnesium oxide that is being observed. In the opinion of Brewer and Kane[22] a low vaporisation coefficient will result when the main gaseous species is a polyatomic molecule that does not exist as such in the condensed phase.

Thermochemical data from Kelley[83] were applied to the reaction

$$CaSO_4(s) = CaO(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \qquad (21)$$

and total pressures of 4×10^{-8} atmospheres at 1000 K and 1.8×10^{-5} atmospheres at 1200 K are to be expected. These values, particularly the second, are fairly close to those found here, see Fig. 19. However the decomposition (21) should be accompanied by a ΔH value of 485 kJ mol^{-1} (116 k cal mol^{-1}) at 1200 K, whereas the results measured here give a value of 223 kJ mol^{-1} (53 k cal mol^{-1}). Reference to Fig. 22 will show that this figure is in closest agreement with that found by Marchal[79] and Zawadski[78] using dehydrated gypsum, namely 260 kJ mol^{-1} (62 k cal mol^{-1}), although their values for the vapour pressure are two orders of magnitude higher. Tschappat and Pièce[77] found a ΔH value of 403.9 kJ mol^{-1} (96.6 k cal mol^{-1}) for the decomposition of anhydrite and dehydrated gypsum, in fair agreement with the calculated value.

The vapour pressures measured in this work are related to the temperature by $\log_{10} P'/\text{torr} = -(0.77 \pm 0.10) \times 10^4 K/T + (4.24 \pm 0.12)$.

With the available thermochemical data a number of alternative schemes were tried. Calculations on the reaction

$$CaSO_4(s) = CaO(s) + SO_3(g) \qquad (22)$$

showed that at 1000 K a total pressure of about 6×10^{-12} atmospheres could be expected and, at 1200 K, 1.3×10^{-8} atmospheres. These values

are far too low for reaction (22) to offer a real alternative to (21). They merely underline that SO_3 is not present in the vapour phase in significant quantities at these temperatures.

The decomposition was carried a stage further in

$$CaSO_4(s) = Ca(g) + SO_2(g) + O_2(g) \qquad (23)$$

Total pressures of 2×10^{-14} atmospheres at 1000 K and 4×10^{-7} atmospheres at 1500 K are once again much too low to be useful here, and in any case the partial pressures of Ca(g), 6×10^{-15} atmospheres at 1000 K and 10^{-7} atmospheres at 1500 K, are much bigger than those required to move the equilibrium

$$CaO(s) \rightleftharpoons Ca(g) + \tfrac{1}{2}O_2(g)$$

to the left, the partial pressure of Ca(g) in this equilibrium being 5×10^{-21} atmospheres at 1000 K and 3×10^{-12} atmospheres at 1500 K.

The only information available on calcium sulphide is its heat of formation, and from this the value of ΔH^{o}_{298} for the reaction

$$CaSO_4(s) = CaS(s) + 2O_2(g)$$

may be deduced as 966 kJ mol^{-1} (231 k cal mol^{-1}); rather too high to help in the immediate problem.

Except for a figure on $CaSO_3 2H_2O$ no information on calcium sulphite could be found.

There remained the possibility of evaporation to monomers of $CaSO_4(g)$. The ionic radii of Ca^{2+} (0.99 Å) and SO_4^{2-} (2.30 Å) yield a radius ratio of 0.430, a good approximation to the ideal for an NaCl type of crystal structure. This means that a Madelung constant of 1.748 is probably applicable to $CaSO_4(s)$. The heat of aggregration of $Ca^{2+}(g)$ and $SO_4^{2-}(g)$ to $CaSO_4(s)$ is in the ratio of 1.748 to 1 to the heat of aggregation to $CaSO_4(g)$ monomers. This means that the heat of sublimation from $CaSO_4(s)$ to $CaSO_4(g)$ may be estimated from 0.748U/1.748 where U = 2704 kJ mol^{-1} (647 k cal mol^{-1}), the lattice energy of calcium sulphate[81]. This gives a value of 1158 kJ mol^{-1} (277 k cal mol^{-1}) which seems to rule out formation of monomers in the vapour phase.

Since some authors find agreement between work done on anhydrite and on dehydrated gypsum whereas others do not, perhaps the history of the sample is significant. Work on calcite has shown that preferential decomposition occurs at some dislocations in deformed crystals[84]. However this would not be expected to make any difference to the overall weight loss.

Tschappat and Pièce declare themselves dissatisfied with Zawadski's proposal that a basic sulphate is formed since the curve of log P vs 1/T does not show a change in direction which would indicate the formation of another compound during dissociation. It is difficult to do other than agree with these authors when they say; "Les valeurs trouvées par Marchal et par Zawadski pour les pressions

de dissociation du gypse déshydraté paraissent inexplicables."

Results and discussion of torsion experiments

This method was attempted for both compounds. The vapour pressure above $CaSO_4$ was too small to give more than one measurable response and details of this are entered below.

T	P
1056 K	2.98×10^{-2} torr

Since this result allied to the corresponding one found by the weight loss method gives a value for the vapour phase molecular weight of rather less than one it is patently unworthy of further consideration.

The results found for magnesium sulphate are shown in Table 11 and Fig. 23. Here it was possible to obtain results over a fairly wide temperature range. Combination with the Knudsen weight loss results yields the following values for the vapour phase molecular weight over $MgSO_4$.

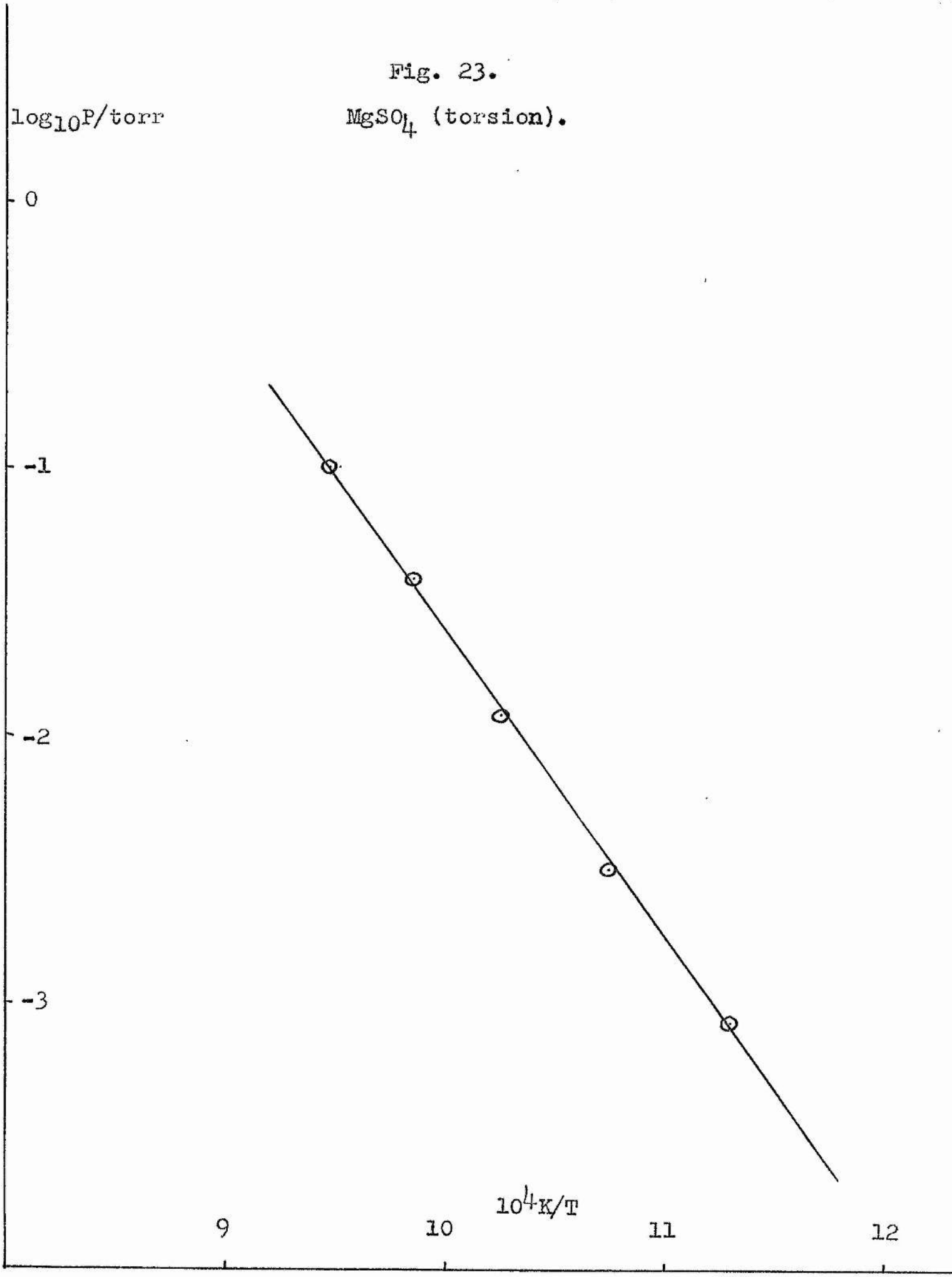
T/K	M
886	42.1
931	57.3
976	57.7
1016	48.2
1056	53.6

Table 11

Magnesium sulphate $MgSO_4$

T/K	P/torr
886	8.46×10^{-4}
931	3.17×10^{-3}
976	1.20×10^{-2}
1016	3.87×10^{-2}
1056	1.01×10^{-1}

Fig. 23.



From these figures the mean molecular weight is 51.8.

If $MgSO_4$ decomposes leaving MgO in the solid phase, then the vapour composition arises from the reaction

$$2SO_3 = 2SO_2 + O_2$$

The average molecular weight of the vapour constituents would therefore be 53.3, in very good agreement with that found here. These results support the view that (20) describes the vaporisation process of magnesium sulphate. The torsion vapour pressure and temperature are related by

$$\log_{10} P/\text{torr} = -1.15 \times 10^4 K/T + 9.94$$

giving a ΔH value of 219 kJ (52.4 k cal) per mole of gas.

This ΔH value compares with that of 225 kJ mol^{-1} found from the graph of the weight loss results. These two values are close enough to support the view that $MgSO_4$ decomposes on heating leaving MgO as a solid phase.

Summary

It would seem that the vaporisation process of magnesium sulphate has been satisfactorily accounted for, although the discovery of the low vaporisation coefficient opens up a new field

of interest. It may be profitable to observe the slow decomposition of a magnesium sulphate crystal by visual, x-ray and perhaps even electron-microscopic methods in an attempt to identify the sites of preferred decomposition. This may be extended to calcium sulphate where results may depend markedly on the history of the starting material and the work described here does not really clarify the situation.

3. Sodium peroxide

Results of Knudsen effusion experiments

The results of the work on sodium peroxide are presented in Table 12 and Fig 24. As may be seen in Fig 24 there is some dependence of the vapour pressure upon the size of the effusion orifice. However since the two smaller holes gave results lying on the same straight line it may be assumed that the equilibrium vapour pressure had been reached at this stage. It was noticed that the edge of the effusion orifice was attacked during the course of a run and also that the entire contents of the cell had evaporated. The point at which this occurred during the run was easily seen when a period of rapid weight loss at high temperature was succeeded by no weight loss at all. The starting material was B.D.H. Microanalytical Reagent grade Na_2O_2.

Blumenthal[71] observed the dissociation of sodium peroxide by Tzentnershver's[85] dynamic method and found the heat of dissociation to be 37.7 k cal mol^{-1}. Apart from this one figure no results of previous experiments on the decomposition of Na_2O_2 could be found for comparative purposes.

Discussion

The equation connecting the vapour pressure and the temperature in this experiment was found to be

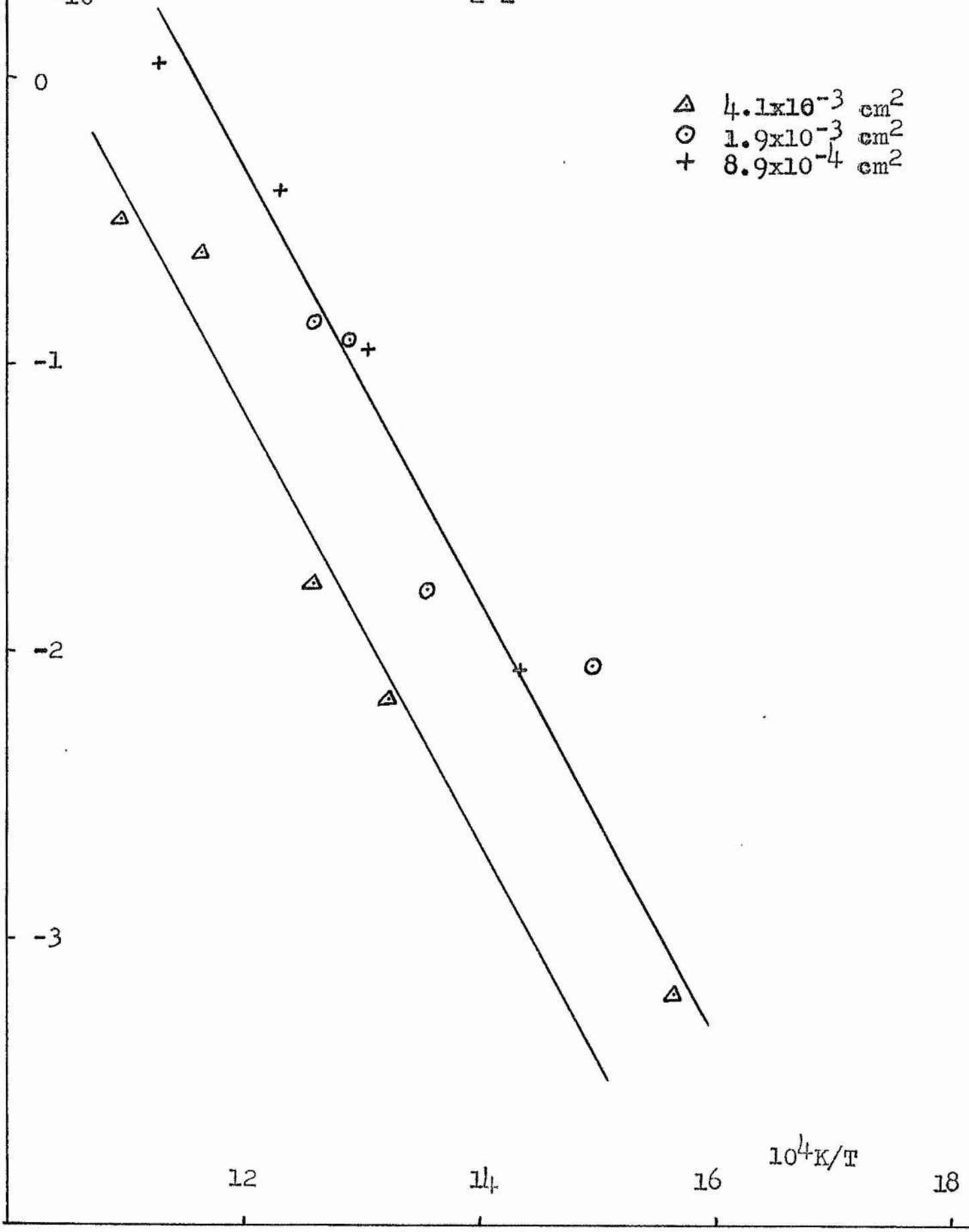
$$\log_{10} P'/\text{torr} = -(0.65 \pm 0.11) \times 10^4 K/T + (7.41 \pm 0.20)$$

Table 12

Sodium peroxide Na_2O_2 (Molecular weight 77.99)

T/K	Rate of wt. loss /mg min^{-1}	P'/torr	Orifice area/cm^2
640	3.15×10^{-3}	6.52×10^{-4}	4.1×10^{-3}
794	0.075	1.73×10^{-2}	
756	0.031	6.86×10^{-3}	
859	1.028	2.46×10^{-1}	
912	1.291	3.19×10^{-1}	
669	1.91×10^{-2}	8.85×10^{-3}	1.9×10^{-3}
776	0.242	1.21×10^{-1}	
794	0.281	1.42×10^{-1}	
738	3.36×10^{-2}	1.63×10^{-2}	
698	8.33×10^{-3}	8.60×10^{-3}	8.9×10^{-4}
766	0.104	1.12×10^{-1}	
812	0.363	4.04×10^{-1}	
886	0.960	1.12	

Fig. 24.


$\log_{10}P'$/torr
Na_2O_2.
0
-1
-2
-3
$4.1x10^{-3}$ cm^2
$1.9x10^{-3}$ cm^2
$8.9x10^{-4}$ cm^2
12
14
16
18
10^4K/T

for the upper graph in Fig 24. The slope of this graph is equivalent to 123.7 kJ mol^{-1} (29.6 k cal mol^{-1}).

An obvious model for the decomposition of Na_2O_2 is the reaction

$$Na_2O_2(s) \rightleftharpoons Na_2O(s) + \tfrac{1}{2}O_2(g) \qquad (24)$$

With the data from the JANAF Thermochemical Tables[80] a number of calculations on this reaction were carried out. ΔH for (24) was found to be 84.8 kJ mol^{-1} (20.3 k cal mol^{-1}) at 1000 K. K_p at 800 K is 1.20×10^{-2} (atmospheres)$^{\frac{1}{2}}$ and at 1000 K is 1.50×10^{-1} (atmospheres)$^{\frac{1}{2}}$. The total pressures corresponding to these values of K_p are about 10^{-4} atmospheres at 800 K and 10^{-2} atmospheres at 1000 K in good agreement with the values measured here. If this model is accepted as accurate the graph gives a ΔH for the reaction of 61.8 kJ mol^{-1} (14.8 k cal mol^{-1}).

The next possibility to be explored was the total decomposition

$$Na_2O_2(s) \rightleftharpoons 2Na(g) + O_2(g). \qquad (25)$$

Calculations on this reaction revealed an expected ΔH of 702 kJ mol^{-1} (168 k cal mol^{-1}) at 1000 K. The value of K_p is 1.3×10^{-26} (atmospheres)^3 at 800 K and 1.6×10^{-17} (atmospheres)^3 at 1000 K with corresponding total pressure values of about 8×10^{-9} and $8 \times 10^{-$ atmospheres respectively. These pressures are very much smaller than those observed here and this reaction does not appear to be significant.

The reaction

$$Na_2O_2(s) \rightleftharpoons 2NaO(g) \qquad (26)$$

was shown, by use of the JANAF data, to have a ΔH value of 594 kJ mol^{-1} (142 k cal mol^{-1}) at 1000 K. The value of K_p for (26) varies between 3.16×10^{-23} (atmospheres)^2 at 800 K and 1.95×10^{-15} (atmospheres)^2 at 1000 K. The corresponding values for the total pressure at these temperatures are about 10^{-11} and 10^{-7} atmospheres. Once again these pressures are too small for reaction (26) to be important here.

The idea of Na(g) being the sole vapour species, formed by the reaction

$$Na_2O_2(s) \rightleftharpoons Na(g) + NaO_2(s) \qquad (27)$$

was investigated with the JANAF data. ΔH for this reaction is 357 kJ mol^{-1} (85.4 k cal mol^{-1}) at 298 K, and the values of K_p are 5×10^{-15} atmospheres at 800 K and 2×10^{-10} atmospheres at 1000 K. The pressures yielded by these values show reaction (27) to be insignficiant.

The lack of available data on $Na_2O(g)$ prohibited a thorough investigation of the reaction

$$Na_2O_2(s) \rightleftharpoons Na_2O(g) + \tfrac{1}{2}O_2(g) \qquad (28)$$

but the circumstantial evidence may be examined. After an investigation of the vaporisation of $Na_2O(c)$ by an effusion method Brewer and Margrave conclude that compared to Na(g) and $O_2(g)$, oxide molecules in the vapour phase are unimportant. However the compilers of the

JANAF tables have used the data reported by Brewer and Margrave[54] to calculate the heat of formation at 298 K for $Na_2O(s)$. They arrive at the value -65.6 k cal mol^{-1} which is somewhat at variance with the value they finally adopt, namely -99.90 k cal mol^{-1}. There is further conflict between the JANAF authors and Bawn and Evans[86] over the heats of formation of NaO and NaO_2. The values of the latter authors are cited by Brewer and Margrave in support of the view that the vapour above solid Na_2O is solely Na(g) and $O_2(g)$.

The dependence of vapour pressure on orifice size mentioned earlier is an indication that the evaporation coefficient of $Na_2O_2(s)$ is small. This may in turn be evidence of a more complex evaporation procedure than merely the release of oxygen from the surface[22,87,88].

If it is assumed for the moment that (28) gives a true picture of the evaporation from $Na_2O_2(s)$ then the value found here for ΔH for the reaction is 186 kJ mol^{-1} (44.5 k cal mol^{-1}). In addition the heat of formation of $Na_2O(g)$ is -324 kJ mol^{-1} (-77.5 k cal mol^{-1}) which allows the calculation of ΔH for the process

$$Na_2O(s) \rightleftharpoons Na_2O(g)$$

to be performed, which yields a value of 91.5 kJ mol^{-1} (21.9 k cal mol^{-1}). In 1935 Preston[89] reported the heat of vaporisation of Na_2O at 1473 K as 38.5 k cal mol^{-1}, Kroger and Stratman[43] found it to be 38.0 k cal mol^{-1} at 1000 K.

Once again the problem of uncertainty in the data for the alkali

metal oxides is evident, but it may be said that reaction (28) remains a real possibility as a description of the evaporation process of $Na_2O_2(s)$, with the decomposition of $Na_2O(g)$ perhaps being inhibited by the presence of oxygen.

4. Sodium metasilicate

Results of Knudsen effusion experiments

The results of the experiments on sodium metasilicate are given in Table 13 and Fig 25. These results show no dependence of vapour pressure on the effusion orifice area. In this case the starting material was only a reagent grade sample.

The results of some work by Kroger and Sorstrom[70] on silicate glasses are useful for comparative purposes and will be examined more critically later.

Discussion

The experimentally determined vapour pressure is related to the temperature by the equation

$$\log_{10} P'/\text{torr} = -(0.68 \pm 0.10) \times 10^4 \; K/T + (3.13 \pm 0.08).$$

From the slope of this graph the ΔH value is 129 kJ mol^{-1} (30.8 k cal mol^{-1}).

A number of possible reaction schemes for the vaporisation of sodium metasilicate will now be considered, culminating in the one

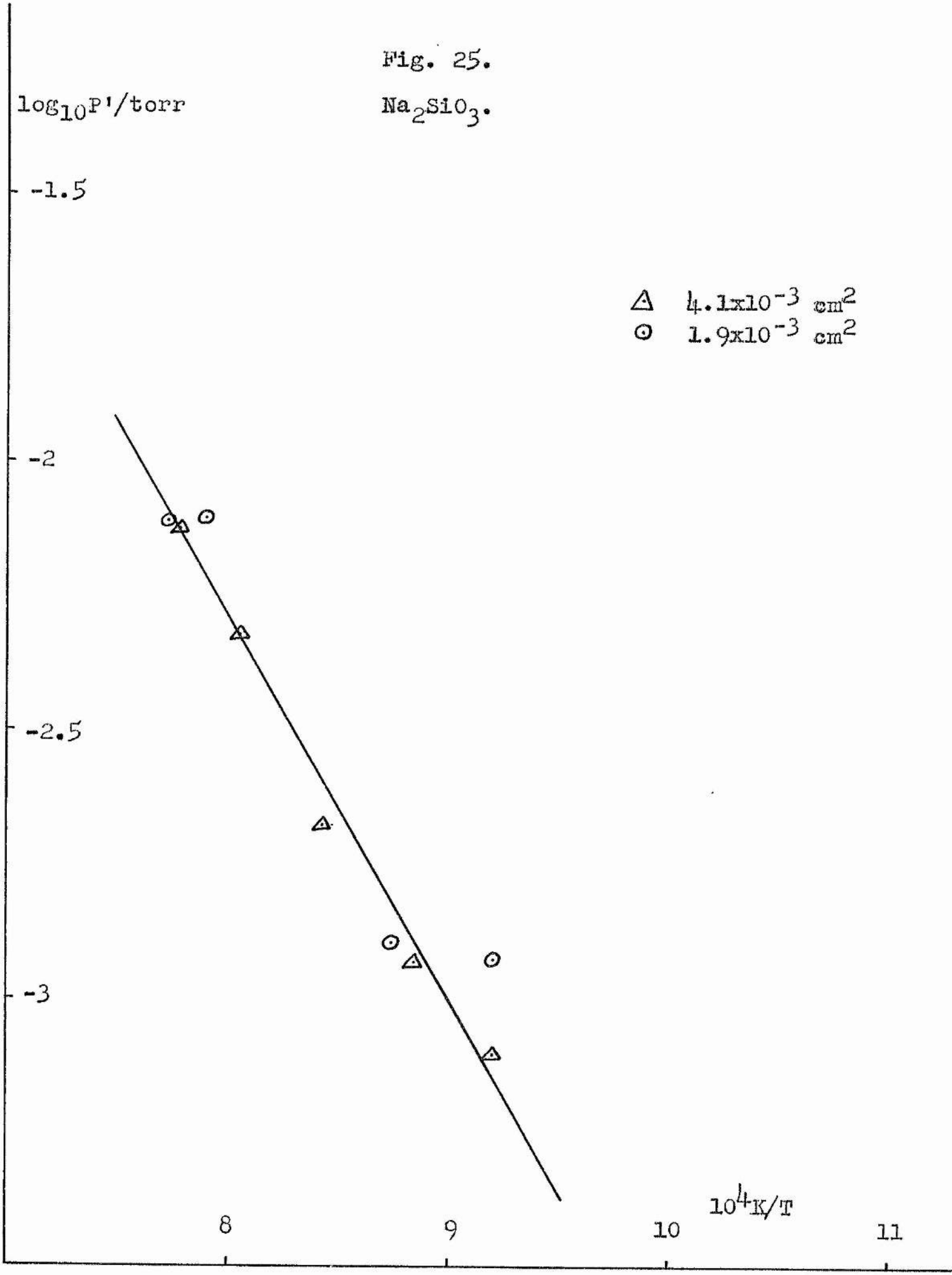
Table 13

Sodium metasilicate Na_2SiO_3 (Molecular weight 122.1)

T/K	Rate of wt. loss /mg min^{-1}	P'/torr	Orifice area/cm^2
1086	3.67×10^{-3}	7.89×10^{-4}	4.1×10^{-3}
1132	5.33×10^{-3}	1.17×10^{-3}	
1186	9.32×10^{-3}	2.10×10^{-3}	
1241	2.07×10^{-2}	4.75×10^{-3}	
1285	3.19×10^{-2}	7.49×10^{-3}	
1087	2.50×10^{-3}	1.18×10^{-3}	1.9×10^{-3}
1144	2.62×10^{-3}	1.27×10^{-3}	
1266	1.53×10^{-2}	7.81×10^{-3}	
1293	1.50×10^{-2}	7.72×10^{-3}	

Fig. 25.

Na_2SiO_3.



thought by Kroger and Sorstrom to be the most probable.

$$Na_2SiO_3(s) \rightleftharpoons 2Na(g) + SiO_2(s) + \tfrac{1}{2}O_2(g) \qquad (29)$$

was examined with the help of the JANAF data and was found to have a ΔH value of 843 kJ mol^{-1} (202 k cal mol^{-1}) at 1200 K. The values of K_p were 1.05×10^{-28} (atmospheres)$^{5/2}$ at 1000 K and 2.14×10^{-21} (atmospheres)$^{5/2}$ at 1200 K, and the total pressure at these temperatures was about 10^{-11} and 10^{-8} atmospheres respectively. These pressures are too low for (29) to represent the main vaporisation process.

Calculations on the reaction

$$Na_2SiO_3(s) \rightleftharpoons Na_2O_2(s) + SiO(g) \qquad (30)$$

reveal a ΔH value of 947 kJ mol^{-1} (226 k cal mol^{-1}) at 298 K and values for K_p of 2.89×10^{-40} atmospheres at 1000 K and 5.76×10^{-32} atmospheres at 1200 K. These figures indicate that this reaction may safely be disregarded.

The decomposition may be taken a stage further to

$$Na_2SiO_3(s) \rightleftharpoons Na_2O(s) + SiO(g) + \tfrac{1}{2}O_2(g) \qquad (31)$$

This reaction was shown to have a ΔH of 1042 kJ mol^{-1} (249 k cal mol^{-1}) at 298 K. The K_p value is 3.47×10^{-41} (atmospheres)$^{3/2}$ at 1000 K and 3.90×10^{-32} (atmospheres)$^{3/2}$ at 1200 K with corresponding values for the total pressure of about 10^{-27} and 10^{-21} atmospheres respectively, indicating that this reaction too is insignificant.

If the heat of formation of $Na_2O(g)$ is taken as -324 kJ mol^{-1} (see previous section) then the formation of the disilicate may be

examined using the JANAF data.

$$2Na_2SiO_3(s) \rightleftharpoons Na_2Si_2O_5(s) + Na_2O(g) \qquad (32)$$

ΔH at 298 K for reaction (32) is 328 kJ mol^{-1} (78.5 k cal mol^{-1}).

In the course of a series of experiments on various Na_2O-SiO_2 systems Kroger and Sorstrom were able to make one measurement of the vapour pressure of the metasilicate below its melting point. On the basis of this value, together with several above the melting point, they conclude that the vapour pressure line becomes less steep above the melting point. They go on to deduce (from the slope of the line below the melting point) a heat of dissociation of 439 kJ mol^{-1} (105 k cal mol^{-1}) for the process

$$Na_2SiO_3(s) \rightleftharpoons Na_2O(g) + SiO_2(s) \qquad (33)$$

which would mean a value of -211 kJ mol^{-1} (-50.5 k cal mol^{-1}) for the heat of formation of $Na_2O(g)$. The slope of the graph above the melting point yields a ΔH of 290.5 kJ mol^{-1} (69.5 k cal mol^{-1}) for the decomposition

$$Na_2SiO_3(l) \rightleftharpoons Na_2O(g) + SiO_2(s) \qquad (34)$$

and consequently a figure of -309 kJ mol^{-1} (-73.9 k cal mol^{-1}) for the heat of formation of $Na_2O(g)$. The difference between these two slopes indicates a heat of fusion of 148 kJ mol^{-1} (35.5 k cal mol^{-1}) which is rather higher than the value quoted in the JANAF tables, namely 12.4 k cal mol^{-1}. If this JANAF value is used, the heat of

dissociation for the process (33) is reduced to 342 kJ mol^{-1} (81.9 k cal mol^{-1}) and the heat of formation of $Na_2O(g)$ becomes -309 kJ mol^{-1} (-73.9 k cal mol^{-1}).

In their Fig 8, Kroger and Sorstrom have plotted values for the heat of dissociation of various sodium silicates to form Na_2O calculated from the known heats of formation of the silicates. This figure gives a value of about 230 kJ mol^{-1} (55 k cal mol^{-1}) at 298 K for the dissociation of $Na_2SiO_3(s)$ which compares closely with that of 234 kJ mol^{-1} (56 k cal mol^{-1}) at 298 K arrived at by using JANAF data for the reaction

$$Na_2SiO_3(s) \rightleftharpoons Na_2O(s) + SiO_2(s) \qquad (35)$$

While acknowledging that this value (55 k cal mol^{-1}) is not strictly comparable to the one they arrive at experimentally (69.5 k cal mol^{-1}), these authors consider them to be close enough to "demonstrate the correctness" of the description of the vaporisation of Na_2SiO_3 in terms of (33).

If the value of the heat of formation of $Na_2O(g)$ is taken as -324 kJ mol^{-1} then ΔH for the process (33) is 326 kJ mol^{-1} (78.0 k cal mol^{-1}).

With the exception of the reactions producing $Na_2O(g)$, all the possible reaction schemes considered above have ΔH values in excess of 200 k cal mol^{-1}, well out of reach of the experimentally determined value. When such small values as 31 k cal mol^{-1} are being considered,

the effect of any uncertainty in the data is enchanced, but it may fairly be said that although the foregoing does not provide a conclusive explanation of the vaporisation of Na_2SiO_3 it does support the value found in the previous section for the heat of formation of $Na_2O(g)$. If the adjusted figure of 342 kJ mol^{-1} (81.9 k cal mol^{-1}) is used as the ΔH value for (33) and the corresponding value for (35) is taken to be 234 kJ mol^{-1} (56 k cal mol^{-1}) then the heat of vaporisation of Na_2O is 108 kJ mol^{-1} (25.9 k cal mol^{-1}). This value is in very good agreement with the one found experimentally and discussed in the previous section, but the ΔH's for both (33) and (34) differ from the value found from the experimental slope for Na_2SiO_3.

Summary of Sections 3 and 4

In section 3, above, a reaction scheme has been put forward to account for the decomposition of Na_2O_2. This scheme receives some support from evidence brought up in the discussion in section 4 on the decomposition of Na_2SiO_3. None of the proposed schemes for the decomposition of Na_2SiO_3 can be fully reconciled with the experimental data measured here; however the wheel has turned full circle and, with the result found (or postulated) here for the heat of formation of $Na_2O(g)$, the reaction

$$Na_2SO_4(s) \rightleftharpoons Na_2O(g) + SO_2(g) + \tfrac{1}{2}O_2(g),$$

first mentioned in the discussion on Na_2SO_4, may be re-examined. With the heats of formation at 298 K found for $Na_2SO_4(s)$ and $SO_2(g)$ in the JANAF tables and the value of -324 kJ mol^{-1} (-77.5 k cal mol^{-1}) used as the heat of formation of $Na_2O(g)$, the ΔH value for the above reaction is calculated as 759 kJ mol^{-1} (181.7 k cal mol^{-1}). This compares rather unfavourably with the value 282 kJ mol^{-1} (67.5 k cal mol^{-1}) found experimentally for Na_2SO_4 at the lower temperatures. This new value of ΔH for the formation of $Na_2O(g)$ permits the examination of a new idea for the vaporisation process of $Na_2SO_4(s)$ along these lines;

$$Na_2SO_4(s) \rightleftharpoons Na_2SO_3(s) + \tfrac{1}{2}O_2(g) \qquad (36)$$

$$Na_2SO_3(s) \rightleftharpoons Na_2O(g) + SO_2(g) \qquad (37)$$

$$Na_2O(g) \rightleftharpoons 2Na(g) + \tfrac{1}{2}O_2(g) \qquad (38)$$

With the heats of formation (at 298 K) for $Na_2SO_4(s)$, $Na(g)$, and $SO_2(g)$ from the JANAF tables and that for $Na_2SO_3(s)$ from Latimer[90], together with the value found here for $Na_2O(g)$, the ΔH values for reactions (36), (37), and (38) are 290.5 kJ mol^{-1} (69.5 k cal mol^{-1}), 469 kJ mol^{-1} (112 k cal mol^{-1}), and 540 kJ mol^{-1} (129 k cal mol^{-1}). If it is assumed that the range of the experimental results reported here covers the first two processes, (36) and (37), then the values calculated above may be compared to those derived from the slopes in Fig. 9. The low temperarure slope gives a ΔH for (36) of

56.4 kJ mol^{-1} (13.5 k cal mol^{-1}), and for the sum of (36) and (37) the high temperature slope gives 564 kJ mol^{-1} (135 k cal mol^{-1}). It can be seen that the low temperature situation is far from being satisfactorily explained by the existing data, but there is now fair agreement between the measured value and the calculated value for the high temperature experimental region. There is some evidence, therefore, for the view that (37) describes part of the vaporisation process of Na_2SO_4.

If the analogous argument is proposed for Li_2SO_4 then the ΔH value for

$$Li_2SO_4(s) \rightleftharpoons Li_2SO_3(s) + \tfrac{1}{2}O_2(g) \qquad (39)$$

is 18 kJ mol^{-1} (4.5 k cal mol^{-1}) from the low temperature graph (Fig. 8). In order to check this by calculation a value must be guessed for the heat of formation of $Li_2SO_3(s)$. -1141 kJ mol^{-1} (-273 k cal mol^{-1}) was chosen by using the same difference between the values for Li_2SO_4 and Li_2SO_3 as exists between the figures quoted for Na_2SO_4 and Na_2SO_3. ΔH for (39) was thus calculated as 293 kJ mol^{-1} (70 k cal mol^{-1}). From the high temperature graph ΔH for

$$Li_2SO_4(s) \rightleftharpoons Li_2O(g) + SO_2(g) + \tfrac{1}{2}O_2(g) \qquad (40)$$

is 552 kJ mol^{-1} (133 k cal mol^{-1}) compared to a calculated value of 970 kJ mol^{-1} (232 k cal mol^{-1}). It may be noted here that the measured figure for ΔH of

$$Li_2SO_4(s) \rightleftharpoons 2Li(g) + SO_2(g) + O_2(g) \qquad (41)$$

is 886 kJ mol^{-1} (212 k cal mol^{-1}) compared with a calculated value of 1459 kJ mol^{-1} (349 k cal mol^{-1}).

Thus the emergence of a figure for the heat of formation of $Na_2O(g)$ has permitted the examination of the vaporisation of $Na_2SO_4(s)$ by a new route, and the analogous case of $Li_2SO_4(s)$ has also been pursued. For the experimental high temperature region the comparison between measured ΔH and calculated ΔH is rather more favourable now for Na_2SO_4 and slightly more favourable even for Li_2SO_4. The low temperature figures for both compounds, but particularly for Li_2SO_4, remain recalcitrant however.

A Critique of the available oxide data

A possible reason for the difficulties experienced here, and by other authors, when attempting explanations of vaporisation phenomena of the alkali metal salts will now be discussed more fully. The common thread running through the labyrinthine discussions of the behaviour of Li_2SO_4, Na_2SO_4, Na_2O_2, and Na_2SiO_3 has been the doubt cast on the validity of some of the data for the alkali metal oxides. The data available on the pure metals Na and Li are probably good for all phases since these substances can be obtained pure and have been available for a long time. For the same reasons the data on Na_2SO_4 and SO_2 are probably reliable. In fact the heat of formation of $Na_2SO_4(s)$ has been measured from the e.m.f. of a suitable cell by Shibata, Oda and Furukawa[91] and the heat capacity by using an adiabatic calorimeter. The heat of sublimation of Li has been measured from the effusion data of Mancherat[92], but in the compilation of the JANAF tables the effusion data of Lewis[93] and Bogros[94] have been disregarded owing to doubtful calibration in Lewis's case and the presence of impurities in both cases. The heat capacity of Li has been determined spectroscopically. The heat of formation of SO_2 has been measured from the heat of combustion of rhombic sulphur. Roth[95] measured the heat of formation of Na_2O_2 (96.81% Na_2O_2, 3.43% Na_2O) utilising its reaction with water, and the same calorimetric method was used by Gillies and Margrave[96] on a purer sample (99.2% Na_2O_2, 0.8% Na_2O). The heat capacity of

Na_2O_2 was measured in a drop calorimeter. Gillies and Margrave also used the reaction of NaO_2 with water in a calorimeter to measure the heat of formation of NaO_2, although the best sample they used contained 4.4% Na_2O_2. The JANAF authors have estimated the heat capacities of NaO_2 above 298 K by comparison with those of Na_2O(s). For LiO(g) the heat of formation has been measured from the mass-spectrometric data of White et al.[97] and the heat capacities using the vibrational frequency and internuclear distance reported by White. It is perhaps an indication of the uncertainty in data derived mass-spectrometrically that the JANAF tables quote the ΔH of formation of LiO(g) as 20.1 $\pm$ 5 k cal mol^{-1}. The compilers of the JANAF tables have calculated the heat of formation of Na_2O(s) from the effusion data of Brewer and Margrave[54] and arrive at a figure of -65.6 k cal mol^{-1}. On the other hand Matsui and Oka[98] and Roth[95], from the heat of reaction of Na_2O(s) with water, found the heat of formation to be -100.2 k cal mol^{-1} (average value). The Matsui sample contained Na_2O_2(s) and Na(s) as impurities, and that of Roth was 3.96% Na_2O_2(s) by weight. The heat capacity of Na_2O(s) was measured by Grimley and Margrave[99] with a copper block, drop-type calorimeter, but the JANAF authors consider Grimley's results at 1078.3 and 1174.6 K to be unreasonably large. Bawn and Evans[86], during a study of the reactions of atomic sodium, arrive at a figure of 13.3 k cal mol^{-1}

for the heat of formation of NaO(g). This quantity is found, spectroscopically, to be 19.4 k cal mol^{-1} by Somayajulu[100] who discovered that for a series of similar diatomic molecules $k_e r_e/D_o$ is constant, where k_e is the force constant, r_e the equilibrium bond distance and D_o the dissociation energy. k_e is calculated from $k_e = 4\pi^2 \nu^2 \mu$ where ν is the vibrational frequency of the diatomic molecule and μ is the reduced mass. The JANAF tables tentatively adopt 20.0 ± 10 k cal mol^{-1} as the heat of formation of NaO(g). In calculations of the heat capacity of NaO(g) the ground state configuration is assumed to be the same as for OH(g), the vibrational frequency is found by comparison with LiO(g), LiF(g), and NaF(g), and the internuclear distance is estimated from OH(g), HF(g), and NaF(g). The heat of formation of Li_2O(s) was found from its reaction with water by Kolesov et al.[101] and from the heat of combustion of Li(s) in oxygen by Fasolino[102]: substantial agreement was reached. The heat of sublimation of Li_2O was found by White[97] from mass-spectrometric data to be 102.5 k cal mol^{-1}. After treatment of the available data on the sublimation of Li_2O the JANAF authors find "relatively large trends of ΔH_s with T which are probably too large to be only due to errors in the functions". Prophet[103] found a heat of sublimation for Li_2O of 50 k cal mol^{-1} after experiments on the decomposition of $LiAlO_2$. The heat capacity of Li_2O(s) has been measured in a drop calorimeter.

Even this brief survey illustrates the contentious nature of some of the available data. In many cases starting materials were impure but in others, NaO, Na_2O_2, Li_2O, most remarkable differences were noted in results found by different methods. To this, of course, may be added the observations, previously noted in the relevant sections, of differences in the results found by mass-spectrometric methods from those found by other methods for K_2SO_4, Rb_2SO_4 and Cs_2SO_4. It is not inconceivable that an undetected agency renders the measurement of absolute quantities by a given method, be it effusion or mass-spectrometric, consistently in error. No reason has yet been advanced, but for the purposes of this discussion it seems fair to say that some data for some compounds should not be accepted unequivocally. No doubt is cast on the reproducibility of the results found during the course of this work, after all, it may be emphasised again that comparable pressures were measured for K_2SO_4, with no break in the line being observed. This short summary of the available oxide data has been included merely to show that a dogmatic acceptance or rejection of a proposed reaction scheme would be incautious if oxide data are used in its interpretation. These data may best be summarised in tabular form as follows.

Compound	ΔH^{o}_{298} formation k cal mol^{-1}	Method of measurement	JANAF adopted value, k cal mol^{-1}
$Li_2O(s)$	(a) -143.1	calorimetric	
	(b) -141.1	Parr bomb	-143.1 ± 0.5
LiO(g)	(a) 22.0	mass-spec.	
	(b) 18.3	mass-spec.	20.1 ± 5
$Na_2O(s)$	(a) -65.6	effusion	
	(b) -100.2	calorimetric	-99.90 ± 1.0
NaO(g)	(a) 13.3	diffusion flame	
	(b) 19.4	spectroscopic	20.0 ± 10
$Na_2O_2(s)$	(a) -121.0	calorimetric	
	(b) -122.66	calorimetric	-122.66 ± 1.2

Compound	ΔH sublimation k cal mol^{-1}	Method of measurement	JANAF adopted value, k cal mol^{-1}
Li_2O	(a) 102.5	mass-spec.	
	(b) 50	decomposition of $LiAlO_2$	
	(c) 101.9	effusion	102.3 ± 3

APPENDIX I

This research arose out of the consideration currently being given to the corrosion suffered by magnesia bricks in the regenerator towers attached to glass-making furnaces. In this concluding section this problem will be examined to see if the results of this work can help towards finding a solution. The worst corrosion takes place at about 1200 K and for this reason the calculations below have been carried out for 1000 K and 1200 K. (For the calculations of equilibrium constants which follow, all the free energy functions were taken from the JANAF Thermochemical Tables.)

Sulphur dioxide features in all the reaction schemes proposed for the vaporisation and decomposition of sodium sulphate, and before the other possible sources of this gas are considered some thought will be given to its action on MgO. The reaction

$$MgO(s) + SO_2(g) = MgSO_3(s) \qquad (43)$$

is one of the few for which free energy function data are not available: however ΔH^o_{298} for (43) is -110.1 kJ mol^{-1} (-26.3 k cal mol^{-1}). The formation of the sulphate by

$$MgO(s) + SO_2(g) + \tfrac{1}{2}O_2(g) = MgSO_4(s) \qquad (44)$$

can be examined in more detail. This reaction has a ΔH^o_{298} of -363.4 kJ mol^{-1} (-86.9 k cal mol^{-1}) and values of K_p of 2.3×10^4 (atmospheres)$^{-3/2}$ at 1000 K and 20.9 (atmospheres)$^{-3/2}$ at 1200 K.

The other possibility considered was

$$MgO(s) + SO_2(g) = MgS(s) + {}^{3}/_{2}O_2(g) \qquad (45)$$

with a ΔH^{o}_{298} value of 550.3 kJ mol^{-1} (131.6 k cal mol^{-1}). K_p values for (45) are 1.9×10^{-25} $(atmospheres)^{\frac{1}{2}}$ at 1000 K and 1.2×10^{-20} $(atmospheres)^{\frac{1}{2}}$ at 1200 K. Of these three possible routes of attack by SO_2 on MgO it seems that only (45) can be ruled out, $MgSO_3$ and $MgSO_4$ are possible reaction products.

Consider now where the available SO_2 has come from. In view of previous discussion one obvious source is

$$Na_2SO_4(s) = 2Na(g) + SO_2(g) + O_2(g) \qquad (46)$$

ΔH^{o}_{298} for this reaction is 1298 kJ mol^{-1} (310.6 k cal mol^{-1}). At 1000 K K_p is 1.1×10^{-38} $(atmospheres)^4$ but at 1600 K it is 2.6×10^{-14} $(atmospheres)^4$. This latter figure indicates a pressure of SO_2 of about 4×10^{-4} atmospheres. SO_2 may be released during the reaction

$$Na_2SO_4(s) + SiO_2(s) = Na_2SiO_3(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \qquad (47)$$

for which ΔH^{o}_{298} is 432.4 kJ mol^{-1} (103.4 k cal mol^{-1}) and K_p is 2×10^{-10} $(atmospheres)^{3/2}$ at 1000 K and 1.7×10^{-2} $(atmospheres)^{3/2}$ at 1600 K. With molten reactants the position is little changed.

$$Na_2SO_4(l) + SiO_2(l) = Na_2SiO_3(l) + SO_2(g) + \tfrac{1}{2}O_2(g) \qquad (48)$$

Now ΔH^{o}_{298} is 450.8 kJ mol^{-1} (107.8 k cal mol^{-1}) and K_p is 7.8×10^{-11} $(atmospheres)^{3/2}$ at 1000 K and 1.9×10^{-2} $(atmospheres)^{3/2}$ at 1600 K,

It may be seen that from both (47) and (48) a pressure of SO_2 of about 0.1 atmospheres may be obtained. A further important source of SO_2 is the combustion products of the fuel oil used to heat the glass batch. It has been calculated[49] that the pressure of sulphur-containing constituents of the gases formed from the oil is 3.5×10^{-3} atmospheres. It is important to remember when looking to (46), (47) and (48) for a source of SO_2 that Na_2SO_4 comprises only 0.5 - 1.0% of the sand weight of the glass batch introduced into the furnace, so that not only is the fuel oil likely to be the major contributor of SO_2 into the furnace atmosphere but SO_2 derived by this means is likely to inhibit the decomposition of Na_2SO_4.

The glass melt in the furnace is heated from above by flames angled down on to the surface; as will be imagined, a good deal of splashing occurs and both liquid drops and hot solids may well be carried over into the regenerator towers. In this way solid and liquid Na_2SO_4, solid and liquid SiO_2, Na_2O, and perhaps even Na may be brought into contact with the MgO bricks. The possibility of reactions occurring will now be discussed.

Consider first the likely reaction

$$MgO(s) + Na_2SO_4(l) = MgSO_4(s) + Na_2O(s) \qquad (49)$$

ΔH^{o}_{298} for this reaction is 277.5 kJ mol^{-1} (66.4 k cal mol^{-1}) and $-\Delta G/T$ is about -326.96 J mol^{-1} deg^{-1} (-78.22 cal mol^{-1} deg^{-1}) at 1000 K and -281.90 J mol^{-1} deg^{-1} (-67.44 cal mol^{-1} deg^{-1}) at 1200 K. If the Na_2O is considered as vaporised, as in

$$MgO(s) + Na_2SO_4(l) = MgSO_4(s) + Na_2O(g) \qquad (50)$$

then ΔH becomes 371 kJ mol^{-1} (89 k cal mol^{-1}). Taken a stage further to

$$MgO(s) + Na_2SO_4(1) = MgSO_4(s) + 2Na(g) + \tfrac{1}{2}O_2(g) \qquad (51)$$

the reaction has a ΔH^{o}_{298} of 910.4 k J mol^{-1} (217.8 k cal mol^{-1}) and values for K_p of 3.9×10^{-34} (atmospheres)$^{5/2}$ at 1000 K and 1.9×10^{-26} (atmospheres)$^{5/2}$ at 1200 K. Reaction (49) has a large negative value for $-\Delta G/T$ and (51) has a very small equilibrium constant which makes them both rather unlikely.

Of the remaining possibly corrosive agents SiO_2 is the next to be examined.

$$MgO(s) + SiO_2(s) = MgSiO_3(s) \qquad (52)$$

ΔH^{o}_{298} - 37.6 kJ mol^{-1} (-9.0 k cal mol^{-1}) $-\Delta G/T$ is about 35.11 J mol^{-1} deg^{-1} (8.40 cal mol^{-1} deg^{-1}) at 1000 K and 28.42 J mol^{-1} deg^{-1} (6.80 cal mol^{-1} deg^{-1}) at 1200 K

$$MgO(s) + SiO_2(1) = MgSiO_3(s) \qquad (53)$$

ΔH^{o}_{298} - 45.1 kJ mol^{-1} (-10.8 k cal mol^{-1}) $-\Delta G/T$ is about 37.58 J mol^{-1} deg^{-1} (8.99 cal mol^{-1} deg^{-1}) at 1000 K and 29.97 J mol^{-1} deg (7.17 cal mol^{-1} deg^{-1}) at 1200 K

$$2MgO(s) + SiO_2(s) = Mg_2SiO_4(s) \qquad (54)$$

ΔH^{o}_{298} -64.4 kJ mol^{-1} (-15.4 k cal mol^{-1}) $-\Delta G/T$ is about 62.78 J mol^{-1} deg^{-1} (15.02 cal mol^{-1} deg^{-1}) at 1000 K and 51.75 J mol^{-1} deg^{-1} (12.38 cal mol^{-1} deg^{-1}) at 1200 K

$$2MgO(s) + SiO_2(1) = Mg_2SiO_4(s) \qquad (55)$$

ΔH^{o}_{298} -71.9 kJ mol^{-1} (-17.2 k cal mol^{-1}) $-\Delta G/T$ is about 65.25 J mol^{-1} deg^{-1} (15.61 cal mol^{-1} deg^{-1}) at 1000 K and 53.29 J mol^{-1} deg^{-1} (12.75 cal mol^{-1} deg^{-1}) at 1200 K. Reactions (52) - (55) represent pathways by which $MgSiO_3$ and Mg_2SiO_4 could be formed by hot SiO_2 from the furnace coming into contact with MgO bricks. It can be seen that all these reactions are feasible but those forming the orthosilicate, (54) and (55), are more favoured. For the sake of completeness in this section the formation of the silicide was examined. The reaction

$$2MgO(s) + SiO_2(s) = Mg_2Si(s) + 2O_2(g) \qquad (56)$$

has a ΔH^{o}_{298} value of 2033 kJ mol^{-1} (486 k cal mol^{-1}) and values for K_p o about 8×10^{-87} (atmospheres)^2 at 1000 K and 4×10^{-69} (atmospheres)^2 at 12

Finally the unlikely chance of elementary sodium reaching the MgO brick can be accounted for together with the equally unlikely formation of Mg in an atmosphere containing some oxygen and abundant nitrogen.

$$MgO(s) + 2Na(g) = Mg(s) + Na_2O(s) \qquad (57)$$

ΔH^{o}_{298} - 32.2 kJ mol^{-1} (-7.7 k cal mol^{-1})

$$MgO(s) + 2Na(g) = Mg(g) + Na_2O(s) \qquad (58)$$

ΔH^{o}_{298} 115.4 kJ mol^{-1} (27.6 k cal mol^{-1})

$$MgO(s) + Na_2O(s) = Mg(g) + Na_2O_2(s) \qquad (59)$$

ΔH^{o}_{298} 653 kJ mol^{-1} (156 k cal mol^{-1})

$-\Delta G/T$ is -510 J mol^{-1} deg^{-1} (-122 cal mol^{-1} deg^{-1}) at 1000 K and -401 J mol^{-1} deg^{-1} (-96 cal mol^{-1} deg^{-1}) at 1200 K

$$MgO(s) + Na_2O(s) = Mg(s) + Na_2O_2(s) \qquad (60)$$

ΔH^{o}_{298} 505 kJ mol^{-1} (121 k cal mol^{-1})

$-\Delta G/T$ is -476 J mol^{-1} deg^{-1} (-114 cal mol^{-1} deg^{-1}) at 1000 K and -393 J mol^{-1} deg^{-1} (-94 cal mol^{-1} deg^{-1}) at 1200 K.

This section may be concluded by a brief assessment of the data presented above. First, there is in the atmosphere passing through the regenerator towers a continuous supply of SO_2 from one source or another, and second, there are also likely to be hot liquids and solids carried over from the melt. The more seriously affected part of the brickwork is at about 1200 K. At this temperature we can see from the above calculations that the formation of MgS and Mg_2Si can be ignored. It also appears that the direct attack of MgO by Na_2SO_4 is very unlikely, but on the other hand MgO may be attacked by SO_2 to form $MgSO_3$ or $MgSO_4$. By far the most favoured of the reactions considered above are those involving silicate formation.

The reaction scheme postulated for the vaporisation and dissociation of Na_2SO_4 in the previous section involves the formation of Na_2O at about the temperature being considered here, but there does not appear to be much reaction along the lines of (59) and (60).

It may be suggested therefore that corrosion takes place principally by the agencies of sulphur dioxide and silicon dioxide with sodium monoxide and sodium sulphate playing a minor role.

Appendix II
Relevant thermodynamic data

1. From JANAF Thermochemical Tables[80].

	$[-(G^o-H^o_{298})/T]$ cal mol^{-1} deg^{-1}				ΔH^o_{298}
	800	1000	1200	1600 K	k cal mol^{-1}
$Li_2O(s)$		17.21	19.61		-143.1
$Li_2O(g)$		61.35	63.17		-39.9
$Li(s)$		10.40	11.34		0
$Li(g)$		35.67	36.33		38.4
$Na_2SO_4(s)$		58.50	64.29	74.58	-330.1
$Na_2SO_4(1)$		63.57	69.35	79.40	-324.2
$Na_2O(s)$	24.59	27.57	30.38		-99.9
$Na_2O_2(s)$	31.21	35.33	38.99		-122.7
$Na_2SiO_3(s)$		43.54	48.31		-373.2
$Na(s)$	15.04	16.20			0
$Na(g)$	38.50	39.24	39.90	41.02	25.75
$MgSO_4(s)$		35.67	39.88		-305.5
$MgO(s)$		11.77	13.28		-143.7
$Mg_2SiO_4(s)$		40.16	45.18		-520.3
$MgSiO_3(s)$		28.17	31.65		-370.2
$SiO_2(s)$		17.00	19.07		-217.5
$SiO_2(1)$		18.21	20.20		-215.7
$SO_3(g)$		68.75	70.91		-94.6
$SO_2(g)$		64.82	66.40	69.17	-70.9
$O_2(g)$	51.63	52.76	53.80	55.61	0

2. From Kelley[83]

$CaSO_4(s)$		39.80	44.27		-342.4
$CaO(s)$		15.27	16.86		-151.9

3. From Latimer[90]

$Na_2SO_3(s)$					-260.6
$Li_2SO_4(s)$					-342.8

1. From JANAF Thermochemical Tables and converted

$[-(G^{o}-H^{o}_{298})/T]$

J mol^{-1} deg^{-1}

	800	1000	1200	1600 K	ΔH^{o}_{298} kJ mol^{-1}
$Li_2O(s)$		71.94	81.97		-598.2
$Li_2O(g)$		256.44	264.05		-166.8
Li(s)		43.47	47.40		0
Li(g)		149.10	151.86		160.5
$Na_2SO_4(s)$		244.53	268.73	311.74	-1379.8
$Na_2SO_4(1)$		265.72	289.88	331.89	-1355.2
$Na_2O(s)$	102.79	115.24	126.99		-417.6
$Na_2O_2(s)$	130.46	147.68	162.98		-512.9
$Na_2SiO_3(s)$		182.00	201.94		-1560.0
Na(s)	62.87	67.72			0
Na(g)	160.93	164.02	166.78	171.46	107.6
$MgSO_4(s)$		149.10	166.70		-1277.0
MgO(s)		49.20	55.51		-600.7
$Mg_2SiO_4(s)$		167.87	188.85		-2174.8
$MgSiO_3(s)$		117.75	132.30		-1547.4
$SiO_2(s)$		71.06	79.71		-909.1
$SiO_2(1)$		76.12	84.44		-901.6
$SO_3(g)$		287.37	296.40		-395.4
$SO_2(g)$		270.95	277.55	289.13	-296.4
$O_2(g)$	215.81	220.54	224.88	232.45	0

2. From Kelley and converted

$CaSO_4(s)$		166.36	185.05		-1431.2
CaO(s)		63.83	70.47		-634.9

3. From Latimer and converted

$Na_2SO_3(s)$					-1089.3
$Li_2SO_4(s)$					-1432.9

References

1. W. Buss, Glastech.Ber., 1962, 35, 167.
2. A.R. Conroy, W.H. Manring and W.C. Bauer, The Glass Industry 1966, 47, 84.
3. M. Knudsen, Ann.Physik, 1909, 28, 999.
4. M. Knudsen, Ann.Physik, 1909, 29, 179.
5. M. Knudsen, Ann.Physik, 1911, 35, 389.
6. P. Clausing, Ann.Physik, 1932, 12, 961.
7. C.I. Whitman, J.Chem.Phys., 1952, 20, 161.
8. K. Motzfeld, J.Phys.Chem., 1955, 59, 139.
9. P.I. Ozhegov and A.M. Evseev, Zh.Fiz.Khim., 1967, 41, 1809.
10. R.D. Freeman and A.W. Searcy, J.Chem.Phys., 1954, 22, 762.
11. E.W. Balson, J.Phys.Chem., 1961, 65, 1151.
12. J.Q. Adams, T.E. Phipps and P.G. Wahlbeck, J.Chem.Phys., 1968, 49, 1609.
13. J.W. Ward and M.V. Fraser, J.Chem.Phys., 1968, 49, 3743.
14. V.I. Lozgachev, Zh.Fiz.Khim., 1963, 37, 644.
15. E.H. Kennard, Kinetic Theory of Gases and Introduction to Statistical Mechanics (McGraw Hill Publ. Co., New York, 1938).
16. G. Mascherpa, Rev.Chim.Minerale, 1966, 3, 153.
17. R.P. Burns, J.Chem.Phys., 1966, 44, 3307.

18. G.M. Rosenblatt, J.Phys.Chem., 1967, 71, 1327.

19. A.N. Nesmeyanov, Vapour Pressures of the Chemical Elements (Elsevier Publ. Co. Ltd., London, 1963).

20. G.M. Rosenblatt and Pang-Kai Lee, J.Chem.Phys., 1970, 52, 1454.

21. G.L. Vidale, U.S. Dept. Com., Office Tech. Serv., PB Rept. 153, 300, 1960.

22. L. Brewer and J.S. Kane, J.Phys.Chem., 1955, 59, 105.

23. R.G. Bautista and J.L. Margrave, J.Phys.Chem., 1965, 69, 1770.

24. R.J. Thorn and G.H.W. Wilson, J.Chem.Phys., 1957, 26, 186.

25. A.R. Miller, J.Phys.Chem., 1967, 71, 1144.

26. E. Kay and N.W. Gregory, J.Phys.Chem., 1958, 62, 1079.

27. P.E. Hart and A.W. Searcy, J.Phys.Chem., 1966, 70, 2763.

28. A.S. Pashinkin, Zh.Fiz.Khim., 1964, 38, 2690.

29. A.S. Pashinkin, Zh.Fiz.Khim., 1966, 40, 2611.

30. A.S. Pashinkin, Zh.Fiz.Khim., 1968, 42, 1511.

31. M.G. Rossman and J. Yarwood, J.Chem.Phys., 1953, 21, 1406.

32. C.I. Whitman, J.Chem.Phys., 1953, 21, 1407.

33. G.A. Komlev, Zh.Fiz.Khim., 1964, 38, 2747.

34. V.G. Muradov, Zh.Fiz.Khim., 1965, 39, 2851.

35. K.Neumann and E. Volker, Z.Phys.Chem., 1932, 161, 33.

36. J.R. McCreary and R.J. Thorn, J.Chem.Phys., 1968, 48, 3290.

37. J.R. McCreary and R.J. Thorn, J.Chem.Phys., 1969, 50, 3725.

38. E.W. Balson, Trans.Far.Soc., 1947, 43, 54.

39. Juey Hong Rai and N.W. Gregory, J.Phys.Chem., 1970, 74, 529.

40. A.W. Searcy and R.D. Freeman, J.Amer.Chem.Soc., 1954, 76, 5229.

41. H. Lindscheid and K.W. Lange, Z. Metallk. 1970, 61, 193.

42. G. Marchal, Bull.Soc.Chim.Fr., 1929, 45, 225.

43. C. Kroger and J. Stratmann, Glastech. Ber., 1961, 34, 311.

44. E. Terres, Brennstoff Chemie, 1954, 35, 225.

45. H. Liander and G. Olsson, IVA, 1937, 4, 145.

46. G. Eyber, Glastech.Ber., 1960, 33, 283.

47. R. Lorenz and W. Herz, Z.anorg.Chem., 1921, 117, 103.

48. R. Bruckner, Glastech.Ber., 1962, 35, 93.

49. M.G. Hocking, private communication to BGIRA.

50. A.A. Fotiev and B.V. Slobodin, Zh.Neorg.Khim., 1965, 10, 569.

51. S. Holmquist, The Glass Industry, 1968, 49, 143.

52. H.H. Kellogg, Trans.A.I.M.E., 1964, 230, 1622.

53. W.H. Manring and W.C. Bauer, Bull.Am.Ceram.Soc., 1965, 44, 405.

54. L. Brewer and J.L. Margrave, J.Phys.Chem., 1955, 59, 421.

55. P.A.H. Wyatt, private communication to BGIRA.

56. P.J. Ficalora, O.M. Uy, D.W. Muenow and J.L. Margrave, J.Am.Ceram.Soc., 1968, 51, 574.

57. M.A. Nettleton and E. Raask, J.Appl.Chem., 1967, 17, 18.

58. T. Kosugi, Kogyo Kagaku Zasshi, 1967, 70, 2089.

59. W.D. Halstead, Trans.Far.Soc., 1970, 66, 1966.

60. J. Dubois and J. Millet, Compt.rend., 1968, 266, 852.

61. F.M. Jaeger, Z.allg.anorg.Chem., 1917, 101, 178.

62. N.M. Hopkin, Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol.II Supplement III (Longmans, 1963).

63. V.I. Spitsyn and V.I. Shostak, Zh.Obshch.Khim., 1949, 19, 1801.

64. K.H. Stern and E.L. Weise, U.S. Nat.Bur.Stand. Report NSRDS-NBS 7 1966.

65. E.W. Dewing and F.D. Richardson, Trans.Far.Soc., 1959, 55, 611.

66. A.G. Ostroff and R.T. Sanderson, J.Inorg. and Nuclear Chem., 1958, 9, 45.

67. J. Cueilleron and O. Hartmanshenn, Bull.Soc.Chim.Fr., 1959, 164.

68. A. Kh. Bronnikov, Izvest.Vysshikh Ucheb.Zavedenii., Khim. i Khim. Tekhnol., 1961, 4, 433.

69. E. Kowalska, Przemyst Chem., 1956, 35, 442.

70. C. Kroger and L. Soerstroem, Glastech.Ber., 1965, 38, 313.

71. M. Blumenthal. Roczniki Chem., 1931, 11, 865.

72. M. Tzentnershver and M. Blumenthal, Bull.Intern.Acad.Polonaise, Classe Sci. Math. Nat., 1933, 499.

73. T.V. Rode and G.A. Gol'der, Izvest.Akad.Nauk S.S.S.R., Otdel Khim. Nauk, 1956, 299.

74. L. Brewer and J.L. Margrave, U.S. Atomic Energy Comm., Natl. Sci. Foundation Washington D.C., 1952, UCRL-1864, 2.

75. S.D. Hill, A. Adams and F.E. Block, U.S. Bur.Mines, Rept. Invest. No. 6849, 1966.

76. H.J. Knopf and H. Staude, Z.Phys.Chem., 1955, 204, 265.

77. C. Tschappat and R. Piece, Helv.Chim.Acta, 1956, 39, 1427.

78. J. Zawadski, Z.anorg.Chem., 1932, 205, 180.

79. G. Marchal, J.Chim.Phys., 1926, 13, 38.

80. JANAF Thermochemical Tables, No. PB-168-370. Edited by D.R. Stull, Dow Chemical Co. Midland, Michigan, 1964.

81. N.M. Selivanova and M. Kh. Karapet'yants, Izvest. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol., 1963, 6, 991.

82. T. Kosugi, Kogyo Kagaku Zasshi, 1970, 73, 1087.

83. K.K. Kelly, U.S. Bur. Mines, 1960, Bull. 584.

84. J.M. Thomas and G.D. Denshaw, J.Chem.Soc.A., 1967, 2058.

85. M. Tzentnershver, J.Chim.Phys., 1930, 27, 9.

86. C.E.H. Bawn and A.G. Evans, Trans.Far.Soc., 1937, 33, 1571.

87. P.G. Wright, Trans.Far.Soc., 1964, 60, 1889.

88. R.D. Shannon, Trans.Far.Soc., 1964, 60, 1902.

89. E. Preston, Trans.Far.Soc., 1935, 31, 776.

90. W.M. Latimer, Oxidation Potentials 2nd ed. (Prentice-Hall 1952).

91. F.L.E. Shibata, S. Oda and S. Furukawa, J.Sci.Hiroshima Univ. (Japan) Ser.A., 1933, 3, 227.

92. M. Mancherat, Compt.rend., 1939, 208, 499.

93. L.C. Lewis, Z. Physik., 1931, 69, 786.

94. A. Bogros, Compt.rend., 1930, 191, 560.

95. W.A. Roth, Z. anorg.Chem., 1948, 255, 324.

96. P.W. Gillies and J.L. Margrave, J.Phys.Chem., 1956, 60, 1333.

97. D. White, K.S. Seshadri, D.F. Dever, D.E. Mann and M.J. Linevsky, J.Chem.Phys., 1963, 39, 2463.

98. M. Matsui and S. Oka, J.Soc.Chem.Ind. (Japan) 1929, 32, 79.

99. R.T. Grimley and J.L. Margrave, J.Phys.Chem., 1960, 64, 1763.

100. G.R. Somayajulu, J.Chem.Phys., 1960, 33, 1541.

101. V.P. Kolesov, S.M. Skuratov and I.D. Zaikin, Russian J.Inorg. Chem., 1959, 4, 558.

102. L.G. Fasolino, Natl. Research Corp. Quarterly Report, July 1 to Sept. 30, 1962.

103. H. Prophet, ARPA-1-150 Dow Chemical Co., Mar. 1961.